GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: October 16, 1978

Project Title: Reuse of Textile Dyeing Wastewater

Project No: E-27-673

Project Director: Dr. Wayne C. Tincher

Sponsor: U.S. Department of the Interior; Office of Water Research and Technology

Agreement Period: From 9/1/78 Until 8/31/80*
*Grant Period of Performance

Type Agreement: Grant 14-34-0001-8813, dtd. 9/7/78

Amount: $64,479 OWRT
7,560 GIT (E-27-320)
$72,039 TOTAL

Reports Required: Quarterly Progress Reports; Summary Report, Final Report

Sponsor Contact Person (s):

Technical Matters

Assistant Director
Research
Office of Water Research
and Technology
U.S. Dept. of the Interior
Washington, D.C. 20240

Contractual Matters
(thru OCA)

Chief
Contracts and Grants Management
Office of Water Research
and Technology
U.S. Dept. of the Interior
Washington, D.C. 20240
Phone (202) 343-6992

Gary D. Cobb
Director, OWRT

Defense Priority Rating: n/a

Assigned to: Textile Engineering (School/Laboratory)

COPIES TO:

Project Director
Division Chief (EES)
School/Laboratory Director
Dean/Director–EES
Accounting Office
Procurement Office
Security Coordinator (OCA)
Reports Coordinator (OCA)

Library, Technical Reports Section
EES Information Office
EES Reports & Procedures
Project File (OCA)
Project Code (GTRI)
Other

CA–3 (3/76)

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 6/7/82

Project Title: Reuse of Textile Dyeing Wastewater

Project No: E-27-673

Project Director: Dr. Wayne C. Tincher

Sponsor: U. S. Department of the Interior; Office of Water Research and Technology

Effective Termination Date: 8/31/80

Clearance of Accounting Charges: 8/31/80

Grant/Contract Closeout Actions Remaining:

- ☐ Final Invoice and Closing Documents
- ☒ Final Fiscal Report
- ☐ Final Report of Inventions
- ☐ Govt. Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Other _____

Assigned to: Textile Engineering (School/Laboratory)

COPIES TO:

Administrative Coordinator	Research Security Services	EES Public Relations (2)
Research Property Management	Reports Coordinator (OCA) ✓	Computer Input
Accounting	Legal Services (OCA)	Project File
Procurement/EES Supply Services	Library	Other _____

FORM OCA 10:781

E 27-673

REUSE OF TEXTILE DYEING WASTEWATER

Quarterly Progress Report #1

September 1, 1978 - November 30, 1978

OWRT Grant No. 14-34-0001-8813

Research Project E-27-673

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia

December 4, 1978

I. INTRODUCTION

Work on the project was initiated on September 1, 1978. In addition to the principal investigator, a research technician (Ms. Lynn Averette) and a graduate student (Mr. Nikolaos Athanasopoulos) were assigned to the project. Principal effort during this period has been devoted to construction of apparatus and development of experimental procedures. Decolorization experiments on a number of important commercial carpet dyes have been carried out.

II. APPARATUS

A laboratory ozone generator and a gas handling system have been constructed to permit exposure of dye solutions to ozone under carefully controlled conditions. The generator is a corona discharge type consisting of two stainless steel screen electrodes separated by a glass tube. The electrode assembly is mounted in a glass pipe to contain and direct a flow of oxygen across the electrodes. The electrodes are connected to a 9 KV tranformer. The generator can produce up to 300 mg of ozone per hour.

Gas from the ozone generator is directed by a stopcock to either of two series of gas bottles equipped with diffusers. In the first line, three gas bottles are filled with potassium iodide solution to trap the ozone generated. The quantity of ozone is determined by the iodometric method in accordance with procedures given in Standard Methods for the Examination of Water and Wastewater. The second series of three gas bottles is used for ozone bleaching of dye solutions. The dye under investigation is placed in the first bottle and potassium iodide solution in the last two gas bottles. The ozone consumed in the dye solution can then be

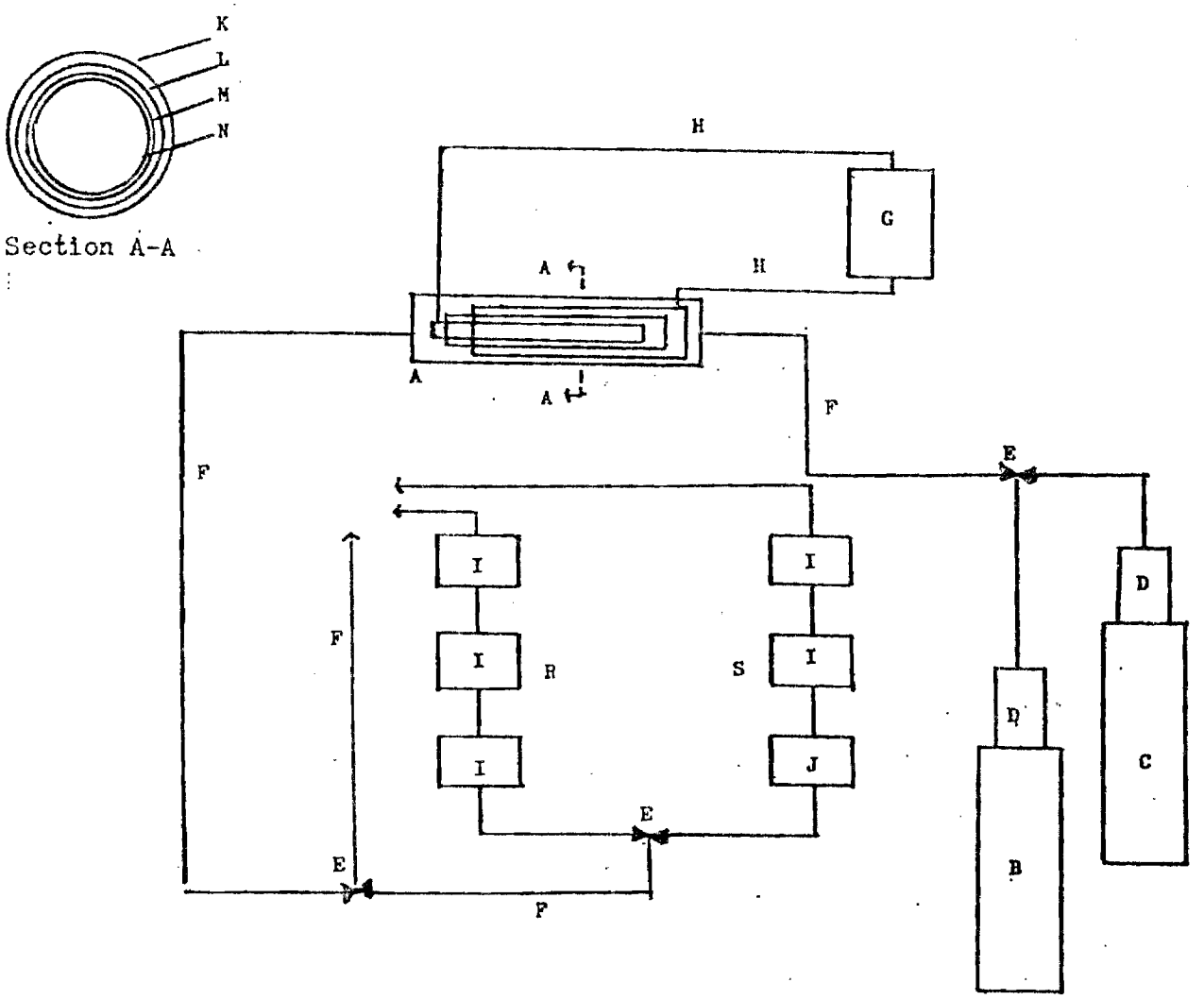
obtained from the known quantity being generated (from the first series) minus the quantity in the stream after the bottle containing the dye solution. A schematic of the apparatus is shown in Figure 1. A number of calibration experiments were conducted to insure that the quantities of ozone in the two series of gas bottles were identical.

III. DYE STANDARDS

Initial studies on ozone decolorization have been carried out on dyes used in large volume in carpet dyeing. Seven dyes--three disperse dyes, three acid dyes and one basic dyes were selected for these studies. Since all commercial dyes contain substantial quantities of impurities, it was necessary to prepare purified dye samples for use as standards. Pure disperse dyes were prepared by Soxhlet extraction with benzene. This procedure was repeated until the absorbance of the dye solution increased to a constant value. Pure acid and basic dyes were prepared by repeated recrystallization from methanol. Usually three recrystallizations were required to achieve a constant absorbance. The quantities of pure dye in the commercial dyes are shown in Table 1.

Standard dye solutions were prepared by dissolving 1 gram of the purified dyes in 1 liter of distilled water. Other concentrations for preparing absorbance versus concentration curves were made by dilution of the 1 gram per liter standard solution.

Concentration of dyes in solution were obtained by absorption spectrophotometry. Standards and/or unknown solutions were placed in a 1 cm quartz cell and the absorbance determined versus a blank at the wavelength of maximum dye absorbance on a Cary Model 219 Spectrophotometer. Since



A	Ozone Generator
B & C	Oxygen and Nitrogen Supply
E	Stopcocks
I & J	Gas Bottles

Figure 1. Schematic Drawing of The Ozonation Apparatus

Table 1. Purity of The Used Dyes

Dye	Wavelength of max. Absorbance (nm)	Concentration ppm	Absorbance		Purity %
			Commercial Dye	Purified Dye	
Celanthrene Fast Blue 2G (Disperse Blue 7)	605	40	.1268	.5797	21.9
Latyl Cerise NSN (Disperse Red 60)	515.5	20	.1054	.8030	13.1
Latyl Yellow YLW (Disperse Yellow 42)	415.5	50	.1296	.7518	17.2
Nylomine Red C-G (Acid Red 151)	511	10	.2860	.7690	37.2
Nylomine Yellow B-2G (Acid Yellow 19)	418	10	.2224	.5156	43.1
Nylomine Blue B-3G (Acid Blue 40)	620	40	.3234	.6366	50.8
Calcozine Yellow C_2G (Basic Yellow 11)	410	10	.2226	.9140	24.4

disperse dyes are not soluble in water, it was necessary to extract the dyes from the water dispersion with benzene and to measure the absorbance of the benzene extract. This procedure has been used previously and has been shown to give accurate analyses of disperse dyes.

IV. DECOLORIZATION EXPERIMENTS

The quantities of ozone required to decolorize each of the seven dyes selected for initial study have been determined quantitatively with the ozone generator and gas handling system described above. Typical results are shown in Figures 2-8. In general, the results show that a quantity of ozone equivalent to the weight of dye in solution is required to decolorize acid and basic dyes. Disperse dyes require much larger quantities of ozone. The difference may be due to chemical structure differences between ionic and disperse dyes or to the fact that disperse dyes are not molecularly dispersed in water. The results certainly suggest that substantial differences in ozone requirements will be necessary in treating different types of dyeing wastewater.

V. FUTURE WORK

During the next quarter the effects of temperature on dye decolorization will be determined. Also the effect of ozone on typical chemical auxiliaries present in carpet dyebaths will be assessed. These data will be important in determining the quantities of chemicals and energy that can be recycled in the reuse experiments. Preliminary dyeing experiments in decolorized wastewater are also planned.

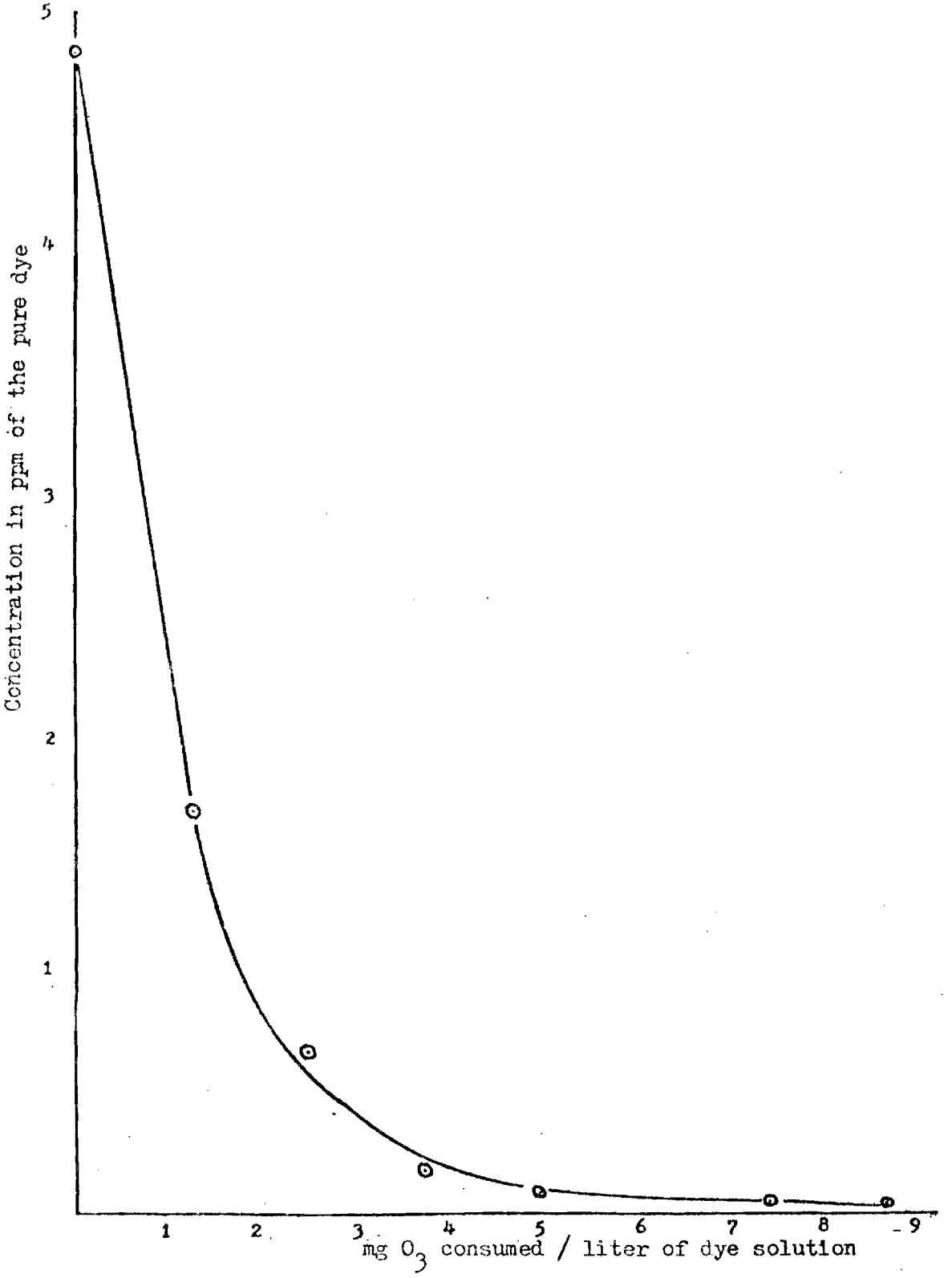


Figure 2. Decolorization of Basic Yellow 11 by Ozone

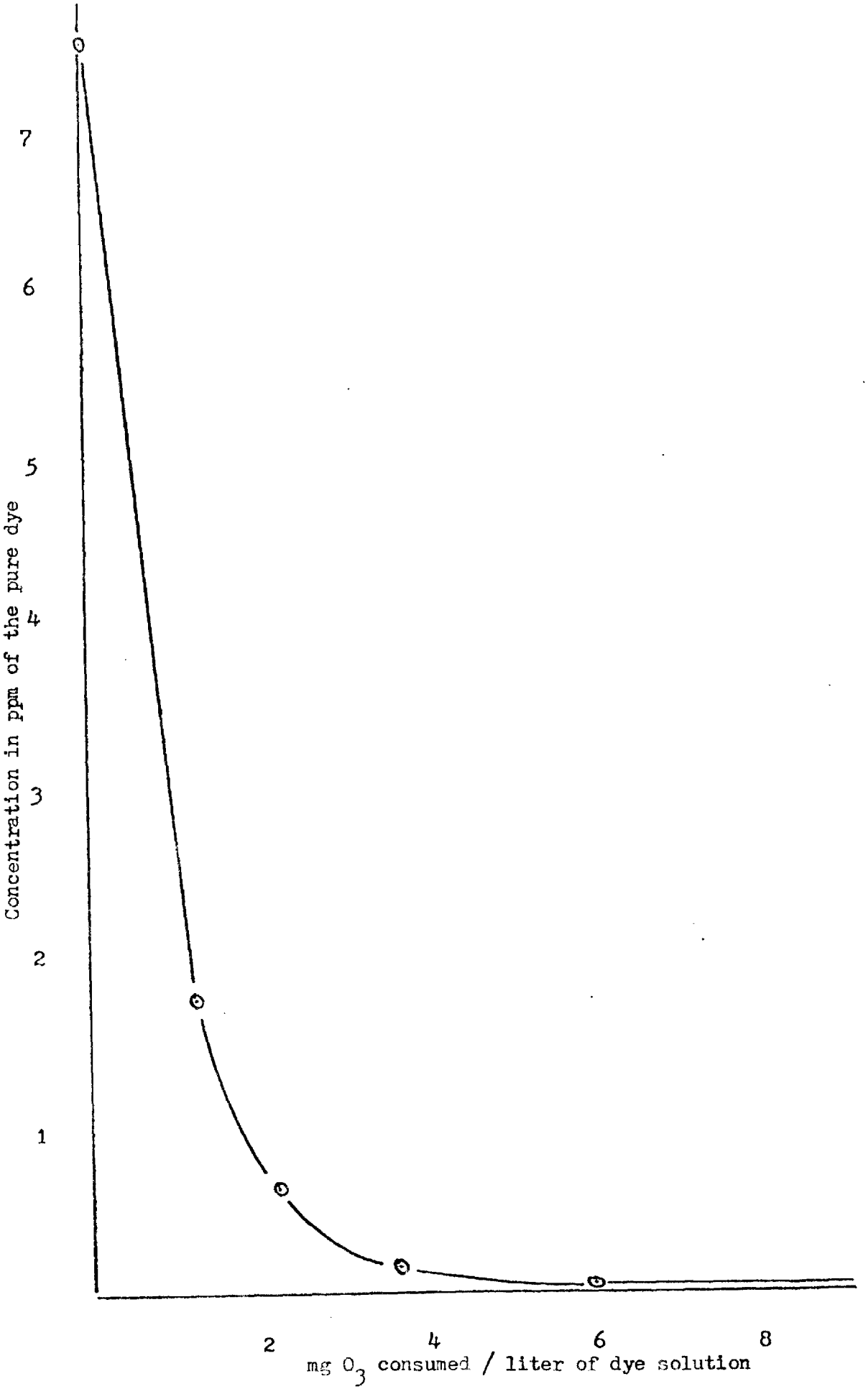


Figure 3. Decolorization of Acid Red 151 by Ozone

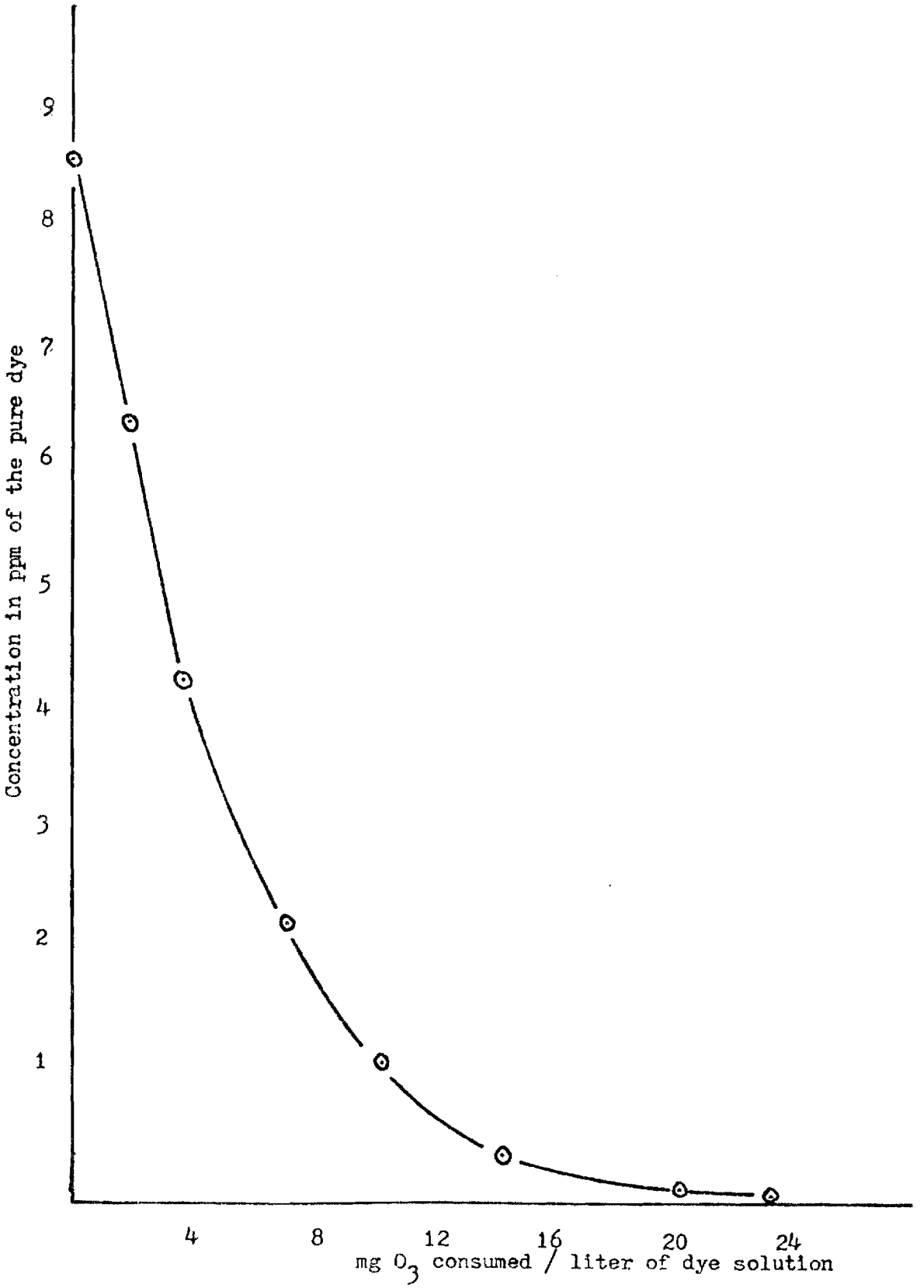


Figure 4. Decolorization of Acid Yellow 19 by Ozone

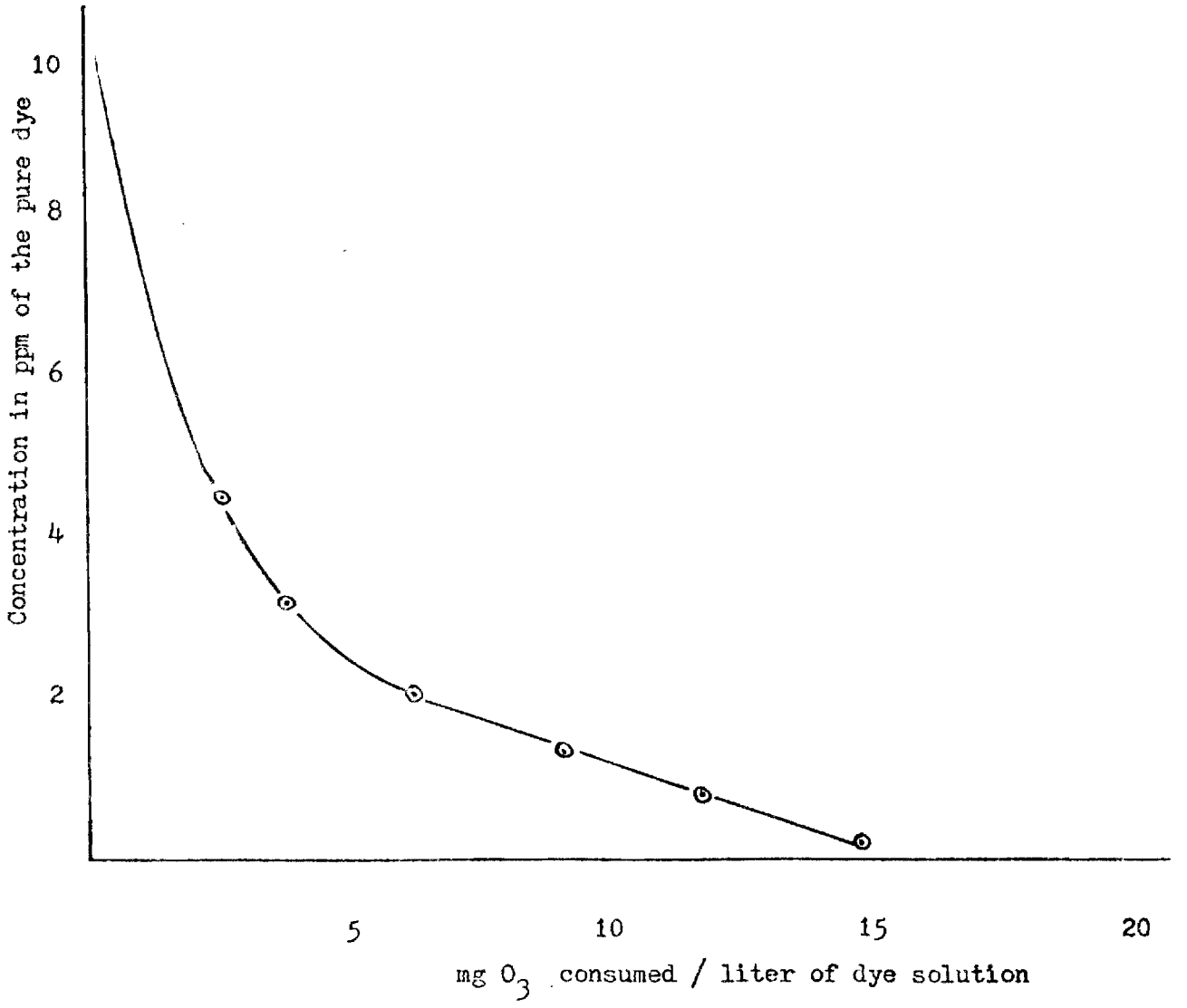


Figure 5. Decolorization of Acid Blue 40 by Ozone

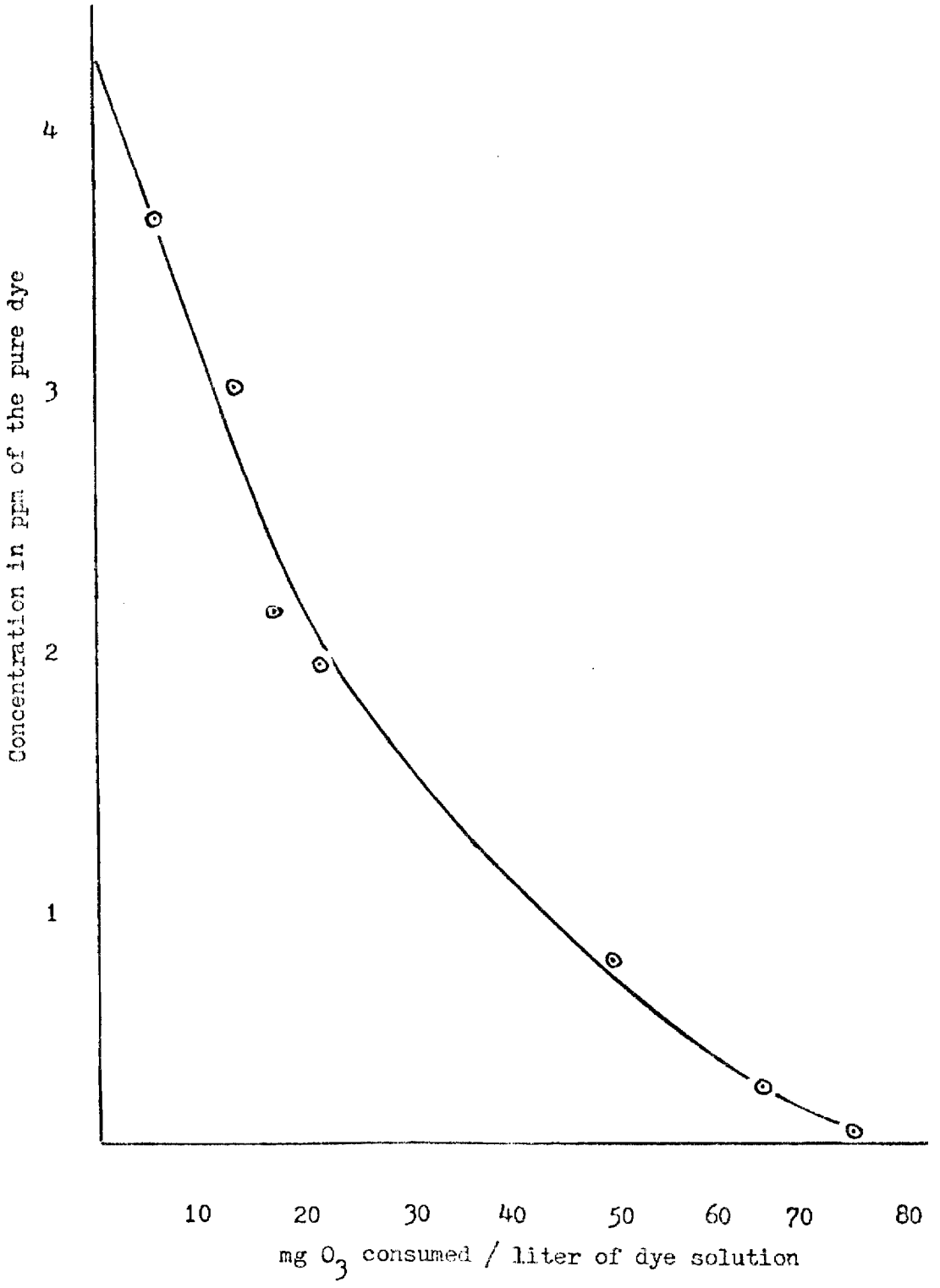


Figure 6. Decolorization of Disperse Blue 7 by Ozone

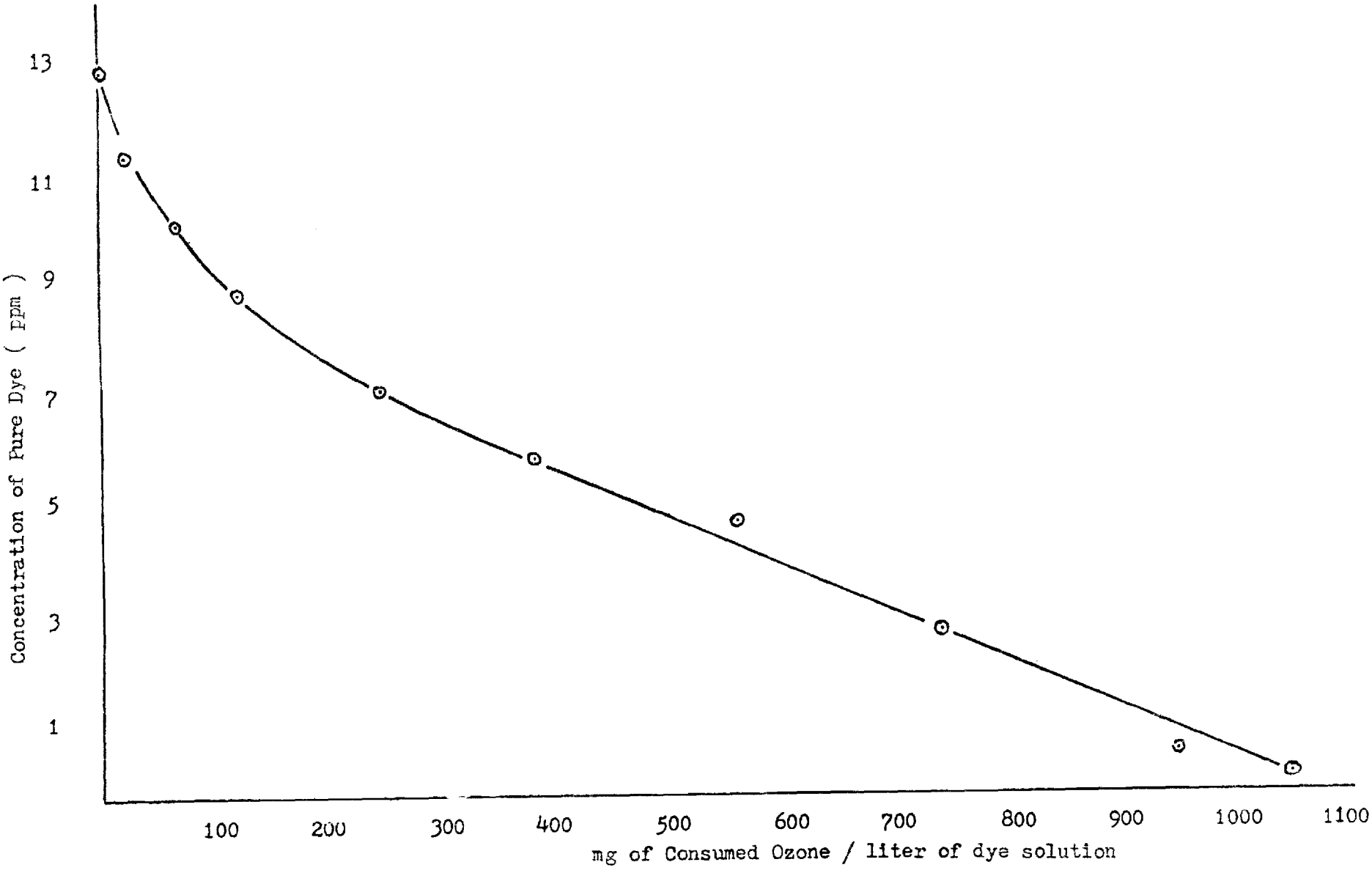


Figure 7. Decolorization of Disperse Yellow 42 by Ozone

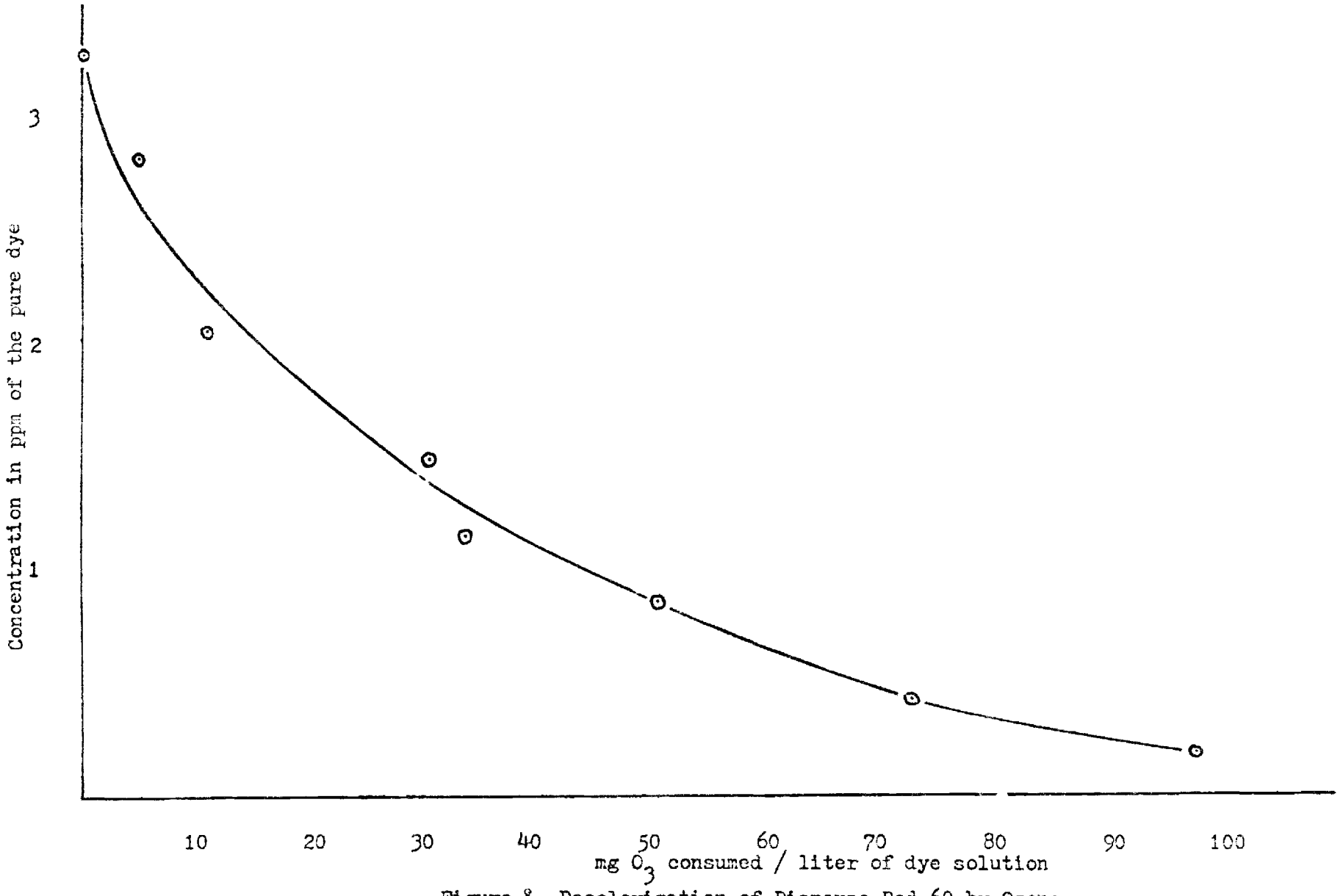


Figure 8. Decolorization of Disperse Red 60 by Ozone

E-27-673

REUSE OF TEXTILE DYEING WASTEWATER

Quarterly Progress Report #2

December 1, 1978 - February 28, 1979

OWRT Grant No. 14-34-0001-8813

Research Project E-27-673

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia

March 5, 1979

I. INTRODUCTION

Principal effort during this quarter has been directed toward expansion of the data base on dye decoloration by ozone and investigation of the effect of temperature on the decoloration rate. Initial dyeing experiments have been carried out with reuse of the dyebath following decoloration.

II. PREPARATION OF ADDITIONAL DYE STANDARDS

Results were reported last quarter on purification and preparation of standards for seven (7) dyes used in large volume in carpet dyeing. An additional fourteen (14) dyes have been purified this quarter to give a total of twenty-one (21) dyes available for ozone decoloration studies. This group of twenty-one dyes represents essentially all the major dyes used in carpet dyeing. The list of dyes is shown in Table 1.

Published methods for dye purification were not successful for several of the acid dyes shown in Table 1. In those cases a new procedure based on adsorption of the dye on macroreticular resin columns and recovery by extraction with organic solvents was used. This technique was developed previously at Georgia Tech to recover dyes from dyeing wastewater. It shows promise as a general method for preparing purified dyes.

III. EFFECT OF TEMPERATURE ON OZONE DECOLORATION

One of the attractive features of decoloration and reuse of dyeing wastewater is the possibility of recycling hot water in the system. Hot water recycle could substantially reduce the quantity of energy required in textile dyeing operations. Recovery of hot water in the recycle system

Table 1

Pure Dyes Prepared for Decoloration and Reuse Studies
(Colour Index Designations)

Acid Yellow 19	Disperse Yellow 3
Acid Yellow 135	Disperse Yellow 23
Acid Yellow 151	Disperse Yellow 42
Acid Yellow 198	Disperse Yellow 54
Acid Orange 128	Disperse Red 55
Acid Red 266	Disperse Blue 7
Acid Red 337	Disperse Blue 26
Acid Blue 25	Disperse Blue 56
Acid Blue 40	Disperse Blue 120

Basic Yellow 11

will require decoloration with selected oxidants at elevated temperatures.

Ozone decoloration experiments have been carried out on several dyes at 80°C. This temperature was selected as representative of the temperature expected in a treatment tank when dyebaths at the boil are discharged to the system. Results of the high temperature ozone treatments are shown in Figures 1, 2 and 3 for Disperse Yellow 42, Acid Blue 40, and Disperse Blue 7.

Results of the high temperature decoloration experiments are very interesting in that both disperse dyes are decolorized more efficiently by ozone at 80°C than at 25°C. The acid dye is decolorized more efficiently at 25°C. It is probable that the greater solubility of disperse dyes at 80°C is responsible for the increased efficiency of decoloration. Disperse dyes exist as aggregates in the dyebath and increasing the solubility would be expected to improve the efficiency of decoloration. Acid dyes, on the other hand, are actually in solution in the dyebath. The decreased solubility of ozone at higher temperatures probably reduces the efficiency of decoloration for acid dyes.

The change in ozone required for acid dye decoloration increased approximately 30% at elevated temperatures. The change in required ozone for disperse dye decoloration was more dramatic, an approximate 40% to 70% reduction. This reduction for disperse dye decoloration is especially significant since disperse dyes require much larger quantities of ozone for decoloration. The reduced ozone demand at the higher temperature should have a very favorable impact on the economics of the decoloration process.

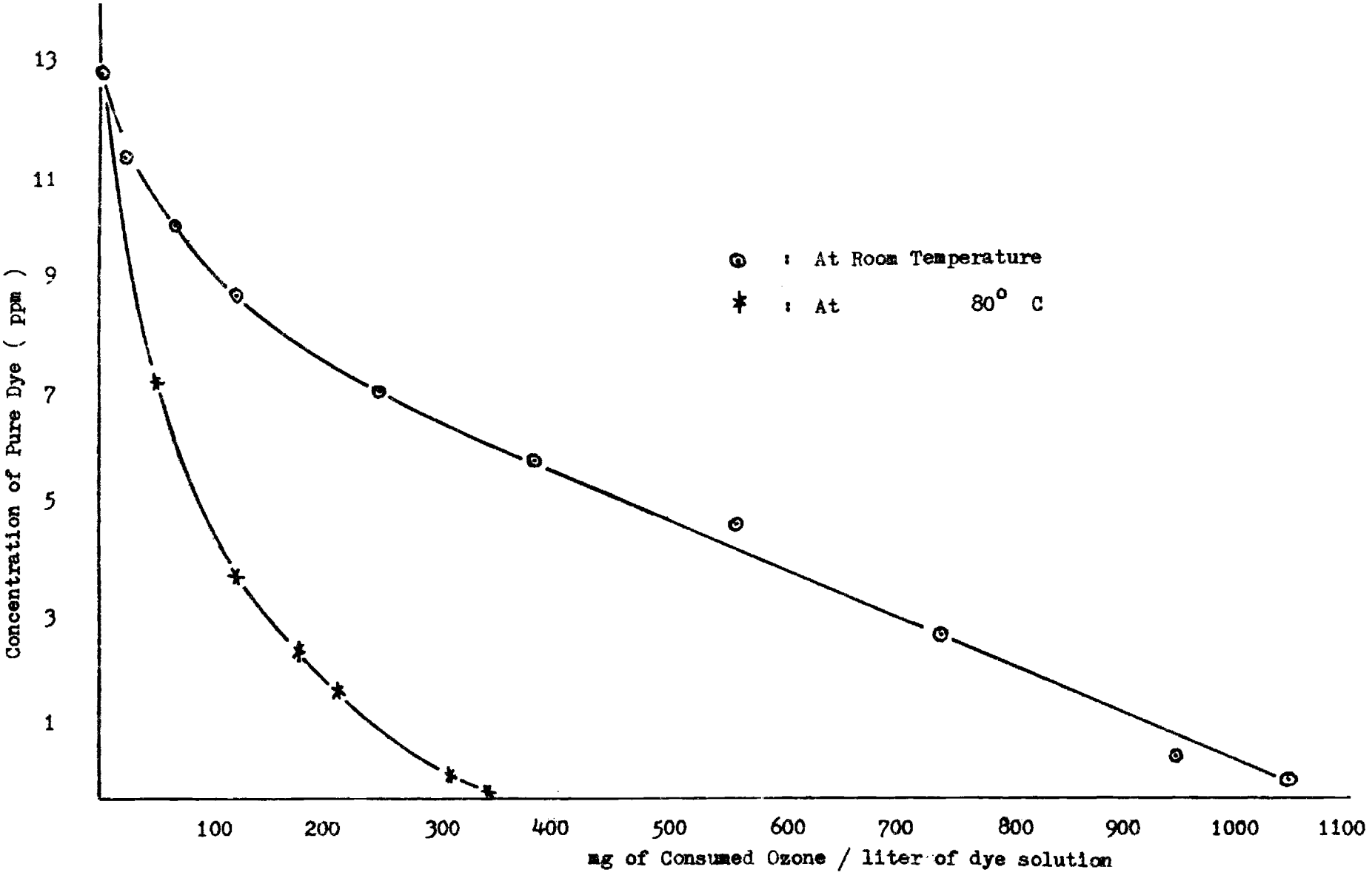


Figure 1. Decolorization of Disperse Yellow 42 by Ozone

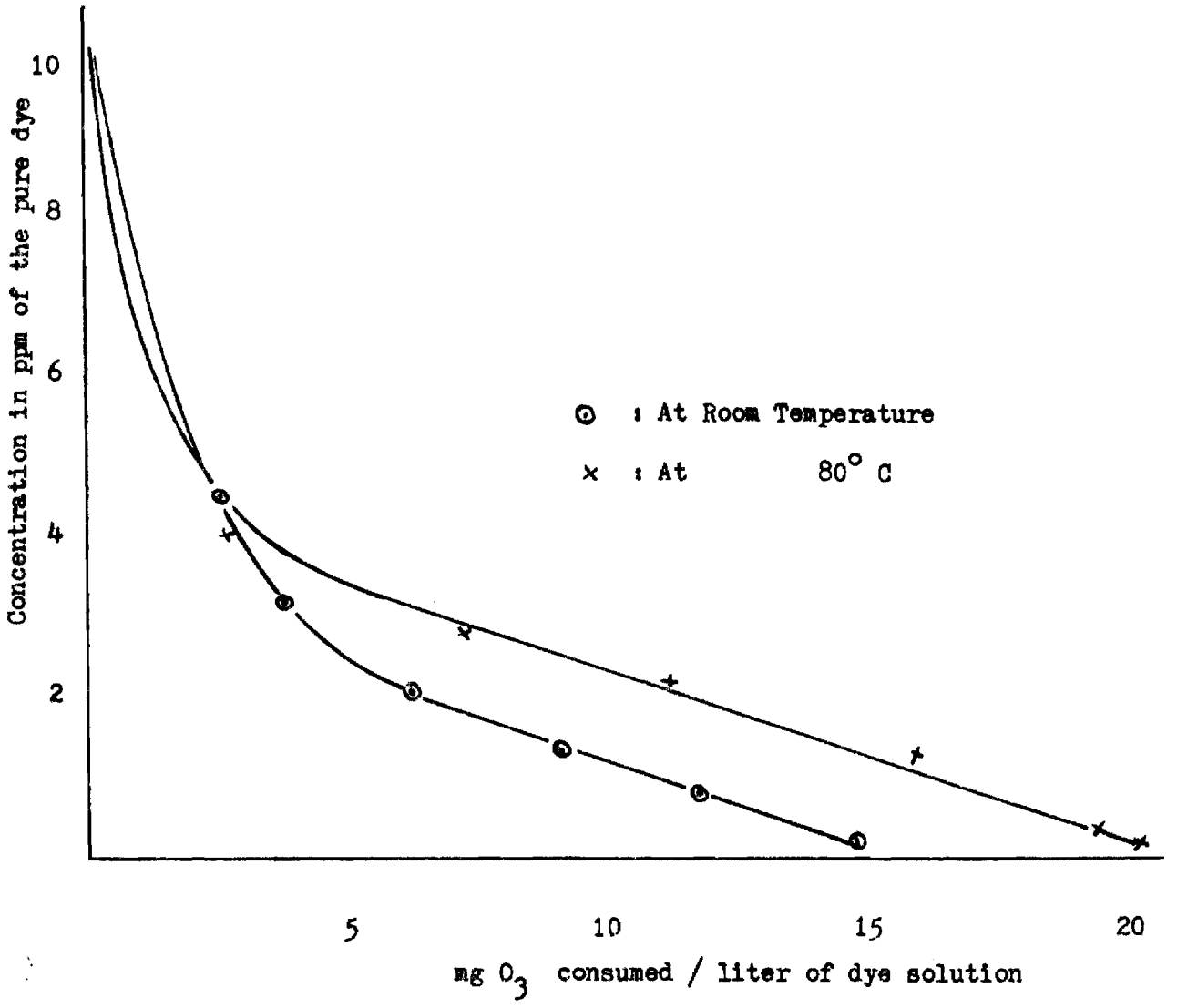


Figure 2. Decolorization of Acid Blue 40 by Ozone

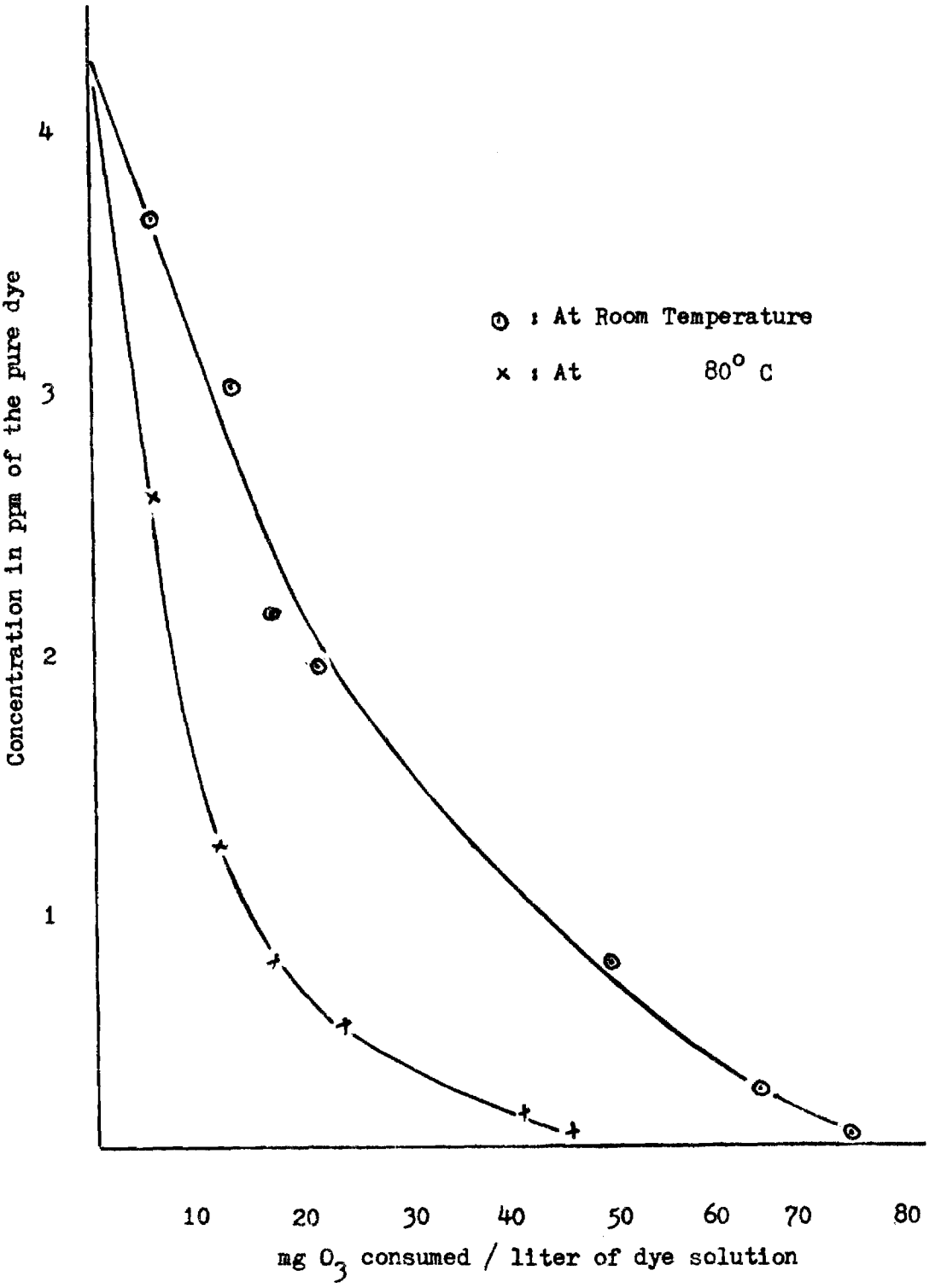


Figure 3. Decolorization of Disperse Blue 7 by Ozone

IV. THE EFFECT OF OZONE ON DYEING AUXILIARY CHEMICALS

In addition to dyes, spent dyebaths will have appreciable quantities of auxiliary chemicals added to control the dyeing process. These chemicals will also react with ozone and the rate of reaction compared to ozone reaction with dyes will be an important consideration in the economic evaluation of ozone decoloration and dyebath reuse.

Two typical auxiliary chemicals were selected for initial study. Avitone T (du Pont) is an anionic surfactant used as a dispersing agent for disperse dyes. Chemcogen 12LD (Chemical Processing of Georgia) is a typical anionic type levelling agent used in acid dyeing of nylon carpets. Results of the exposure of these two auxiliary chemicals to ozone at room temperature (25°C) are shown in Table 2 and Figure 4. The quantities of the surfactants in the control and ozone treated solutions were determined using the methylene blue active substances procedure (Standard Methods for Examination of Water and Wastewater).

Results of the study of effects of ozone on auxiliary chemicals were encouraging since they indicate that these types of compounds react more slowly with ozone than the dyes. They should, therefore, have a low ozone demand during dye decoloration and substantial quantities of the auxiliary chemicals should be recyclable in the process.

V. INITIAL DYEING EXPERIMENTS

Nylon carpet samples dyed with a mixture of acid and basic dyes was selected for initial studies.

A large piece of nylon carpet was prescoured to remove fiber lubricants, identification tints, etc. A 50 gram sample of the carpet was

Table 2. Ozone Oxidation of The Surfactants

Active Substance	mg of O_3 Consumed per liter	Absorbance in 652 nm	Concentration ppm
Chemcogen 12-LD	0.0	.0858	500.0
	23.0	.0807	455.9
	42.4	.0778	431.2
	59.5	.0706	368.4
	80.0	.0681	347.1
Avitone T	0.0	.0722	500.0
	64.0	.0714	494.5
	130.3	.0680	471.0
	202.0	.0644	446.0
	236.4	.0592	408.0

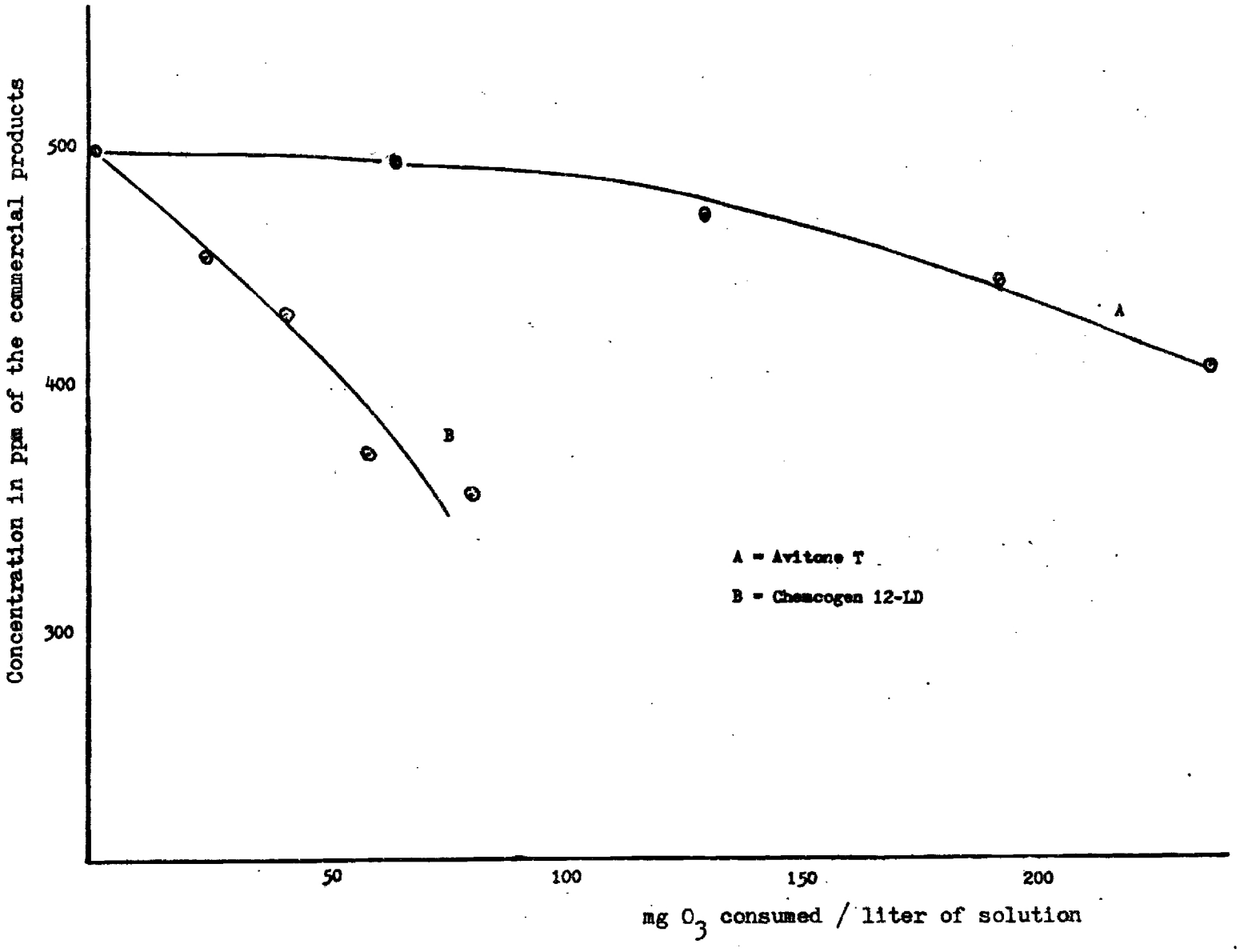


Figure 4 . Oxidation of Chemcogen 12-LD and Avitone T by Ozone

placed in a 5-liter beaker and 1.5 liters of water (liquor ratio of 30:1) were added. A levelling agent, Chemcogen 12LD (0.5 grams or 1% owf), and pH control agent, monosodium phosphate (0.5 g or 100% owf) were added. A few drops of an antifoaming agent, Nofome HS (Chem-Mark, Inc.) were also added. The following dyes were used:

Acid Red	0.0115 g	(0.023% owf)
Acid Blue 40	0.0160 g	(0.0327% owf)
Basic Yellow 11	0.1750 g	(0.35% owf)

The temperature was raised to 100°C at 2°C per minute and held at 100°C for fifteen (15) minutes. Acetic acid was added to adjust the pH to 4.5 and the dyeing continued for thirty (30) additional mintues. The carpet was removed from the beaker and rinsed and afterscoured.

The residual dyebath of 1050 ml (after losses due to evaporation and water removed with the carpet) was then exposed to ozone to decolorize the residual dyes. The quantities of ozone required are given in Table 3. The dyebath was used for five (5) consecutive dyeings before being discarded. As indicated in Table 3, the quantity of ozone actually required for the dyebath decoloration was very close to the amount calculated from the residual dye concentration and the ozone dye decoloration curves previously obtained.

Samples dyed in the recycled baths are now being evaluated.

VI. FUTURE WORK

Further analysis of the samples of nylon carpet dyed in the ozone decolorized and recycled baths is planned for next quarter. Dyeing of polyester carpet in decolorized and recycled baths is also planned.

Table 3. Decolorization of Waste Dyebaths of Nylon Carpet Dyeings

No of Dyeing	Absorbance after Dyeing			Conc. of Pure Dye ppm			Decolorization %			Calculated O_3	Actual O_3
	410nm	511nm	620 nm	Red	Blue	Yellow	Red	Blue	Yellow	Required mg/l	consumed mg/l
1	.1271	.0115	.0098	.12	.62	1.31	100	100	98	3.3	3.9
2	.1831	.0063	.0018	.07	.14	1.95	100	100	99	3.4	4.2
3	.2880	.0060	.0016	.06	.14	3.08	100	100	100	5.6	6.0
4	.3229	.0062	.0022	.06	.18	3.45	100	100	100	6.3	7.4
5	.3348	.0052	.0021	.05	.18	3.58					

REUSE OF TEXTILE DYEING WASTEWATER

Quarterly Progress Report No. 3

March 1, 1979 - May 31, 1979

OWRT Grant No. 14-34-0001-8813

Research Project E-27-673

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia

June 5, 1979

I. Introduction

Major effort this quarter has been directed toward evaluation of nylon carpet samples dyed in decolorized and recycled dyebaths. Initial dyeing experiments on polyester carpet have also been conducted.

II. Evaluation of Samples Dyed in Recycled Dyebaths

Last quarter, five samples of nylon carpet were dyed consecutively in the same dyebath by decolorizing with ozone and reuse of the bath. These samples have been evaluated for color reproducibility, stability of the color to light exposure (lightfastness), colorfastness to water exposure, and colorfastness to abrasion (crockfastness). Standard exposure conditions and evaluation procedures were used to assess the quality of the dyeings in recycled baths.

A. Color Reproducibility

Instrumental measurements of color were used to assess the between sample color variation in the dyeings. A Diano LSCE Automate color measuring instrument was used for color measurement.

In color measurement on the samples of nylon carpet dyed with acid and basic dyes it was necessary to make measurements on yarn removed from the carpet. This was done because the differentially dyeable nylon fibers gave different colors when

dyed with acid and basic dyes and the differently dyed areas in the carpet were not large enough for direct measurement on the Automate. The individual yarns were removed and wrapped loosely and uniformly around strong rectangular white paper in such a way that all the surface was covered by the loose yarns. For each sample six measurements were obtained, three in a horizontal position and three in a vertical position of the yarns. The average of these six measurements (expressed as the tristimulus values, X, Y, and Z) was taken as the tristimulus values for each sample. The first conventionally dyed carpet was taken as the standard.

Color differences between the first dyeing (in a fresh bath) and the 4 subsequent dyeings (in the recycled bath) were calculated using the Friele-MacAdam-Chickering equation (FMC-II). In this system 1 unit of color difference is a just perceptible color difference to the average observer. Results of the color difference calculation for the regular nylon yarn and the nylon yarn that dyes with the basic dye are shown in Table 1.

The color difference values, DE, in Table 1 are of the order of 2 or 3 FMC-II units. This agrees quite favorably with typical color differences encountered in carpet production. In general, color differences as large as 5 FMC-II units are considered acceptable matches in carpet dyeing. Thus, all of the dyeings in recycled baths were within acceptable limits for first quality carpet production.

Table 1.

Color Data on Reproducibility from Run to Run

SAMPLE	TRISTIMULUS VALUES X	Y	Z	DE
Acid Dyed Nylon Std. No. 1	31.91	29.10	29.05	---
Sample No. 2	31.96	29.18	30.06	3.3
No. 3	31.46	30.23	29.86	3.8
No. 4	31.76	29.31	29.14	3.9
No. 5	31.04	28.09	29.00	3.0
Basic Dyed Nylon Std.No. 1	56.13	58.82	14.98	---
Sample No. 2	57.46	60.54	14.45	3.6
No. 3	56.97	59.56	14.55	2.8
No. 4	56.53	59.13	14.00	3.8
No. 5	56.60	58.96	14.42	3.7

B. Crockfastness

Colorfastness to rubbing (crocking) was evaluated by the American Association of Textile Chemists and Colorists (AATCC) Test Method Number 8. Carpet samples were cut oblique to the warp and weft directions of the carpet backing and subjected to 20 cycles on a standard Crockmeter. The evaluation of color transfer was conducted by means of the AATCC Chromatic Transference Scale. Results of the colorfastness to crocking test are shown in Table 2. It is clear that the samples dyed in recycled baths are identical to the conventional dyeing run.

C. Colorfastness to Water

The method for testing fastness to water was AATCC Test Method 107. The test was carried out as per specificiations in the AATCC Technical Manual, except for the fact that multifiber Test Fabric No. 10 (containing spun acetate, bleached cotton, spun nylon 66, spun Dacron 54, spun Orlon 75, worsted wool) was used instead of multifiber Fabric No. 1 (containing spun acetate, bleached cotton, spun nylon 66, spun silk, spun viscose, worsted wool). Plexiglass plates of specified dimensions were used between specimens. The evaluation of fastness was done by means of the AATCC Gray Scale for Staining.

Result of the colorfastness to water test are shown in Table 3. Again, the samples dyed in recycled baths show similar behavior to conventional dyeing.

Table 2.

Evaluation of Fastness to Dry Crock

CARPET	RUN NO.	RATINGS
Nylon, Regular	1	5
	2	5
	3	5
	4	5
	5	5
Nylon, Basic Dyeable	1	5
	2	5
	3	5
	4	5
	5	5

Table 3.

Evaluation of Fastness to Water

CARPET	RUN NO.	RATINGS
Nylon	1	4
	2	4
	3	4-5
	4	4-5
	5	4-5

D. Colorfastness to Light

Lightfastness was evaluated by AATCC Test Method 16F, which is the testing of colorfastness to continuous light from a water-cooled xenon-arc lamp. The samples were exposed to the light source for 20,40,60,80,100, and 120 hours. The light fastness was evluated by comparing the differences between exposed and unexposed strips of the sample with the AATCC Gray Scale for Color Change.

Result of colorfastness to light tests are shown in Table 4. The conventionally dyed sample and samples dyed in recycled baths show similar lightfastness properties.

E. Summary of Evaluation Tests

Based on reproducibility of color and colorfastness properties, samples of nylon carpet dyed in dyebaths decolorized with ozone and reused show properties equivalent to similar properties of a conventionally dyed sample. Thus, quality of dyeings does not appear to be affected by use of recycled baths.

III. Initial Polyester Carpet Dyeings

Polyester carpet samples have been dyed with disperse dyes in a manner similar to the nylon carpet dyeings described previously. A large piece of polyester carpet was prescoured to remove fiber lubricants, identification tints, etc. A 50 gram sample of the carpet was placed in a 5-liter beaker and 1.5 liters of water (liquor ratio of 30:1) were added. A dye dispersing agent, Avitone T (0.5 grams or

Table 4.

Evaluation of Lightfastness

CARPET	RUN NO.	HOURS OF EXPOSURE					
		20	40	60	80	100	120
Nylon, Regular	1	4-5	4	3	1-2	1	1
	2	5	3-4	3	1-2	1	1
	3	5	4	3	1-2	1	1
	4	5	4	3-4	1-2	1	1
	5	5	4	3-4	1-2	1	1
Nylon, Basic Dyeable	1	5	4-5	4	3-4	3-4	3
	2	5	4-5	4-5	4	3-4	3
	3	5	5	4-5	4	4	3-4
	4	5	4-5	4-5	4-5	4	3-4
	5	5	5	4-5	4	3-4	3-4

1% owf), a pH control agent, monosodium phosphate (1.0 gram or 20% owf) and a few drops of an antifoaming agent, Nofome HS, were added. The following dyes were used:

Disperse Yellow 42	0.170% owf	or	0.085 grams
Disperse Red 60	0.020% owf	or	0.010 grams
Disperse Blue 7	0.030% owf	or	0.015 grams

The pH was adjusted to 5.0 with acetic acid and a dye carrier, Carolid L-65, (10% owf or 5 grams) was added. The temperature was raised to 100°C and maintained for 1 hour. The carpet sample was then removed from the beaker, rinsed with warm water, afterscoured, and dryed at 120°F for 1 hour.

The used dyebath (1050 ml) was then exposed to ozone to decolorize the residual dyes. The bath was then reconstituted to its original volume and used for the next dyeing. Five dyeings were carried out in the same bath.

Ozone consumption for decolorization of the spent dyebaths are shown in Table 5. As noted for the nylon carpet dyeings, the actual ozone requirements were very similar to the calculated requirements based on dye decolorization experiments carried out earlier.

The polyester carpet samples are now being evaluated.

IV. Future Work

Evaluation of the polyester carpet samples dyed in decolorized and recycled dyebaths will be carried out next quarter.

Table 5.

Decolorization of Waste Dyebaths of Polyester Carpet Dyeings

NO. OF DYEING	ABSORBANCE AFTER DYEING			COMM. DYE CONCENTR. ppm			DECOLORIZATION %			Calculated O_3 Required mg/l	Actual O_3 Consumed mg/l
	415.5nm	515.5nm	605nm	Red	Blue	Yellow	Red	Blue	Yellow		
1	.0341	.0051	.0170	1.38	5.59	26.25	100	100	96	379.0	414.6
2	.0270	.0062	.0134	3.04	4.39	20.69	100	100	94	300.5	332.7
3	.0306	.0077	.0131	4.71	4.27	23.52	100	100	95	347.1	380.2
4	.0264	.0065	.0176	2.42	5.77	19.96	100	100	92	288.0	323.2
5	.0272	.0054	.0119	2.47	3.90	20.96	100	100	95	302.9	330.1

Reuse of Textile Dyeing Wastewater

Intermediate Progress Report

September 1, 1978 to August 31, 1979

OWRT Grant No. 14-34-0001-8813

Research Project E-27-673

Wayne C. Tincher

School of Textile Engineering

Georgia Institute of Technology

Atlanta, Georgia

November 26, 1979

I. INTRODUCTION

The textile industry uses and discharges approximately 150 billion gallons of water annually. Much of this wastewater contains substantial quantities of suspended and dissolved organic compounds which can have an adverse effect on receiving streams. Dyes present in textile processing wastewater are resistant to usual wastewater treatment procedures and constitute a particularly difficult problem.

The objective of this research project is to determine the technical and economic feasibility of recycling textile dyeing wastewater by decolorization with ozone and/or "singlet" oxygen. Decolorization of textile wastewater in this way should permit recycling, not only of the water, but also a substantial part of the auxiliary chemicals used in the dyeing process. Reduced chemical cost could offset, therefore, a substantial part of the treatment cost.

II. EXPERIMENTAL PROCEDURES

A. Dyes and Auxiliary Chemicals

The dyes selected for study were dyes commonly used for carpet coloration. A list of dyes in the initial studies is given in Table 1. Since all commercial dyes contain substantial quantities of impurities, it was necessary to prepare purified dye samples for use as standards. Pure disperse dyes were prepared by Soxhlet extraction with benzene. This procedure was repeated until the absorbance of the dye solution increased to a constant value. Pure acid and basic dyes were prepared by repeated recrystallization from methanol. Usually three recrystallizations were required to achieve a constant absorbance.

Table 1

Pure Dyes Prepared for Decoloration and Reuse Studies
(Colour Index Designations)

Acid Yellow 19	Disperse Yellow 3
Acid Yellow 135	Disperse Yellow 23
Acid Yellow 151	Disperse Yellow 42
Acid Yellow 198	Disperse Yellow 54
Acid Orange 128	Disperse Red 55
Acid Red 266	Disperse Blue 7
Acid Red 337	Disperse Blue 26
Acid Blue 25	Disperse Blue 56
Acid Blue 40	Disperse Blue 120

Basic Yellow 11

Chemical Auxiliaries

Surfactant - Tanapon SC (Tanatex)

pH Control Agents - Tetrasodiumpyrophosphate

- Monosodium phosphate

Leveling Agent - Chemcogen 12-D (Chemical Processing of Georgia)

Dispersing Agent - Avitone T (du Pont)

Carrier - Carolid - L-65 (Tanatex)

Antifoaming Agent - Nofome HS (Tanatex)

Published methods for dye purification were not successful for several of the acid dyes shown in Table 1. In those cases a new procedure based on adsorption of the dye on macroreticular resin columns and recovery by extraction with organic solvents was used. This technique was developed previously at Georgia Tech to recover dyes from dyeing wastewater. It shows promise as a general method for preparing purified dyes.

Standard dye solutions were prepared by dissolving 1 gram of the purified dyes in 1 liter of distilled water. Other concentrations for preparing absorbance versus concentration curves were made by dilution of the 1 gram per liter standard solution.

Concentration of dyes in solution were obtained by absorption spectrophotometry. Standards and/or unknown solutions were placed in a 1 cm quartz cell and the absorbance determined versus a blank at the wavelength of maximum dye absorption on a Cary Model 219 Spectrophotometer. Since disperse dyes are not soluble in water, it was necessary to extract the dyes from the water dispersion with benzene and to measure the absorbance of the benzene extract. This procedure has been previously used and has been shown to give accurate analyses of disperse dyes.

The chemical auxiliaries used in dyeing experiments are also given in Table 1. The chemical auxiliaries are types commonly employed in dyeing nylon and polyester carpets.

B. Equipment

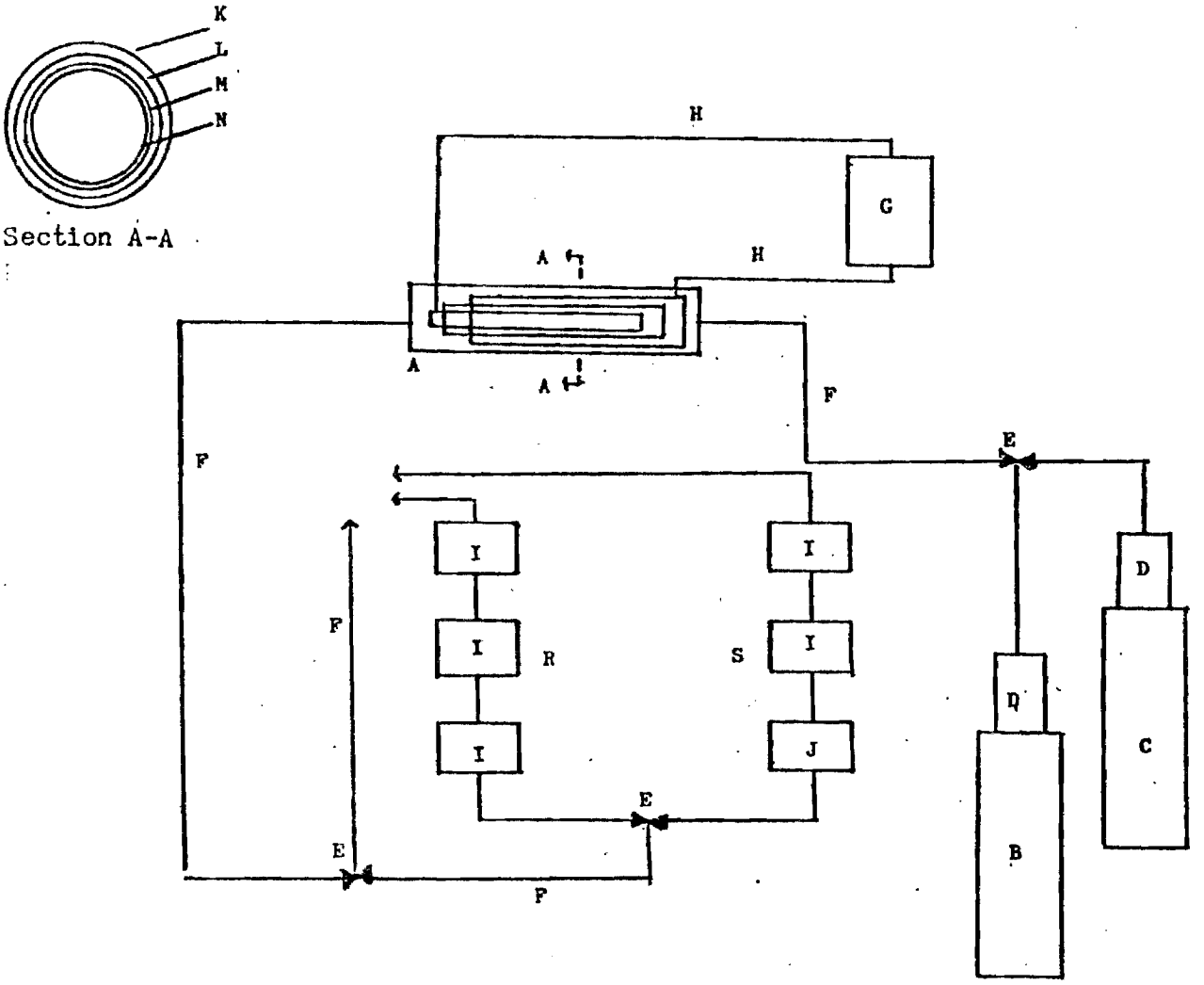
1. Ozonator

A small ozone generator was constructed for the dye decolorization experiments. A schematic drawing of the ozone unit and gas handling

system is shown in Figure 1. Two stainless steel screens (L and N) 16" long, provided by Custom Scientific Instrument, Inc., in tube form and separated with a glass dielectric tube (m) of thickness 1.2 mm, were used as high voltage electrodes. The electrodes and dielectric were fixed in the glass tube (K). Two stainless steel wire electrodes (H) were sealed in the outer glass tube. A 9 kilowatt transformer (G) was used for developing the high voltage required for discharge.

Tygon tubing (f), which is resistant to ozone, was used for transfer of ozone from the discharge tube (A) to the gas wash bottles (I,J). Gas wash bottles of 250 ml and 1500 ml with porous difusers were used for sample oxidizing and ozone trap in one series (S) and for reference ozone consumption in a second series (R). Extra dry oxygen or nitrogen was fed to the ozonator from the cylinders (B) and (C) at a constant rate of flow with the help of the two regulators (D). Changing of the feeding gas to the ozonator and of the flow of ozone to one or to the other series of gas wash bottles was carried out through the three way stopcocks (E). The discharge tube (A) was air sealed by using two O-ring glass joints in the two ends locked to the tube with two screw locking devices. An electric timer was used for measuring the intervals of exposure of the sample and reference solutions to ozone.

Part of the oxygen passing through the ozonator was converted to ozone. The mixture of ozone and oxygen was fed through the tygon tubing to the reference bottles which contained a standard solution of potassium iodide or to the sample bottle which contained the sample to be oxidized and to the trapping bottles which contained the same iodide solution as the reference bottles. The amount of ozone consumed by the sample solution



A	Ozone Generator
B & C	Oxygen and Nitrogen Supply
E	Stopcocks
I & J	Gas Bottles

Figure 1. Schematic Drawing of The Ozonation Apparatus

was calculated by the difference of free iodine production in the reference and trapping bottles.

To determine the accuracy of this procedure, the amount of ozone fed into the two series of bottles was measured 10 times in the beginning of the work using in both series of bottles only potassium iodide. The difference in ozone production in all these experiments or the error of the procedure was less than one percent. The production of ozone by the ozonator was about 300 mg per hour. For the decolorization curves for dyes and the oxidation curves for surfactants 250 ml bottles were used. For the decolorization of the waste dyebaths 1500 ml bottles were used.

2. Other Equipment

A Cary Model 219 Recording Spectrophotometer was used for analysis of the dye concentrations in all decolorization studies. A Corning Model 12 pH meter was used for measurement and control of pH in all dyeings. Color measurements on dyed samples were made on a DIANO/LSCE Color Instrument. Stability of dyeings to light and abrasion were determined using an Atlas Xenon-Arc Fade-O-Meter and a Crockmeter (American Association of Textile Chemists and Colorists), respectively.

C. Dye Decolorization Experiments

The quantities of ozone required to decolorize each of the seven dyes selected for initial study have been determined quantitatively with the ozone generator and gas handling system described above. Typical results are shown in Figures 2-8. In general, the results show that a quantity of ozone equivalent to the weight of dye in solution is required

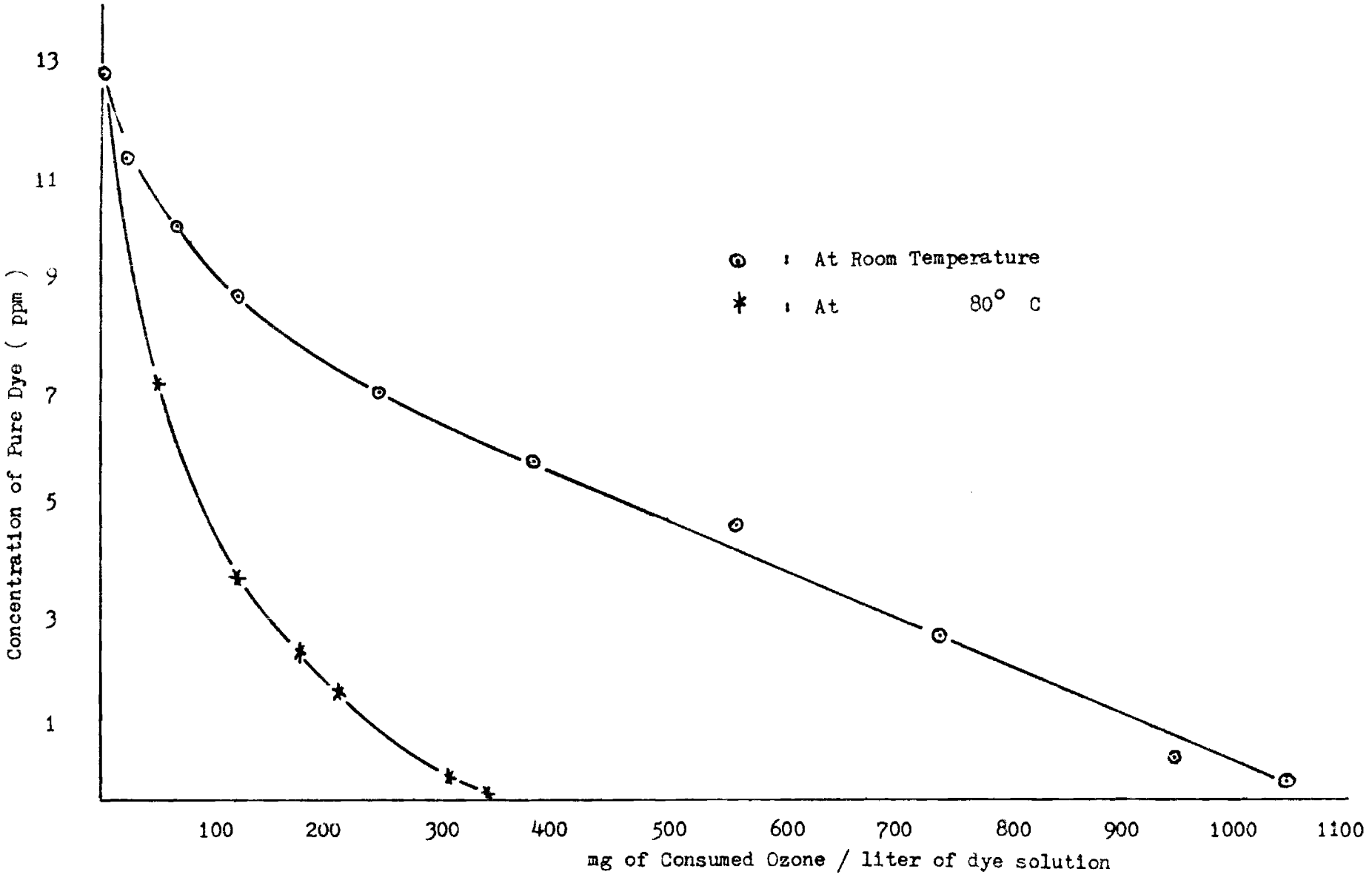


Figure 2. Decolorization of Disperse Yellow 42 by Ozone

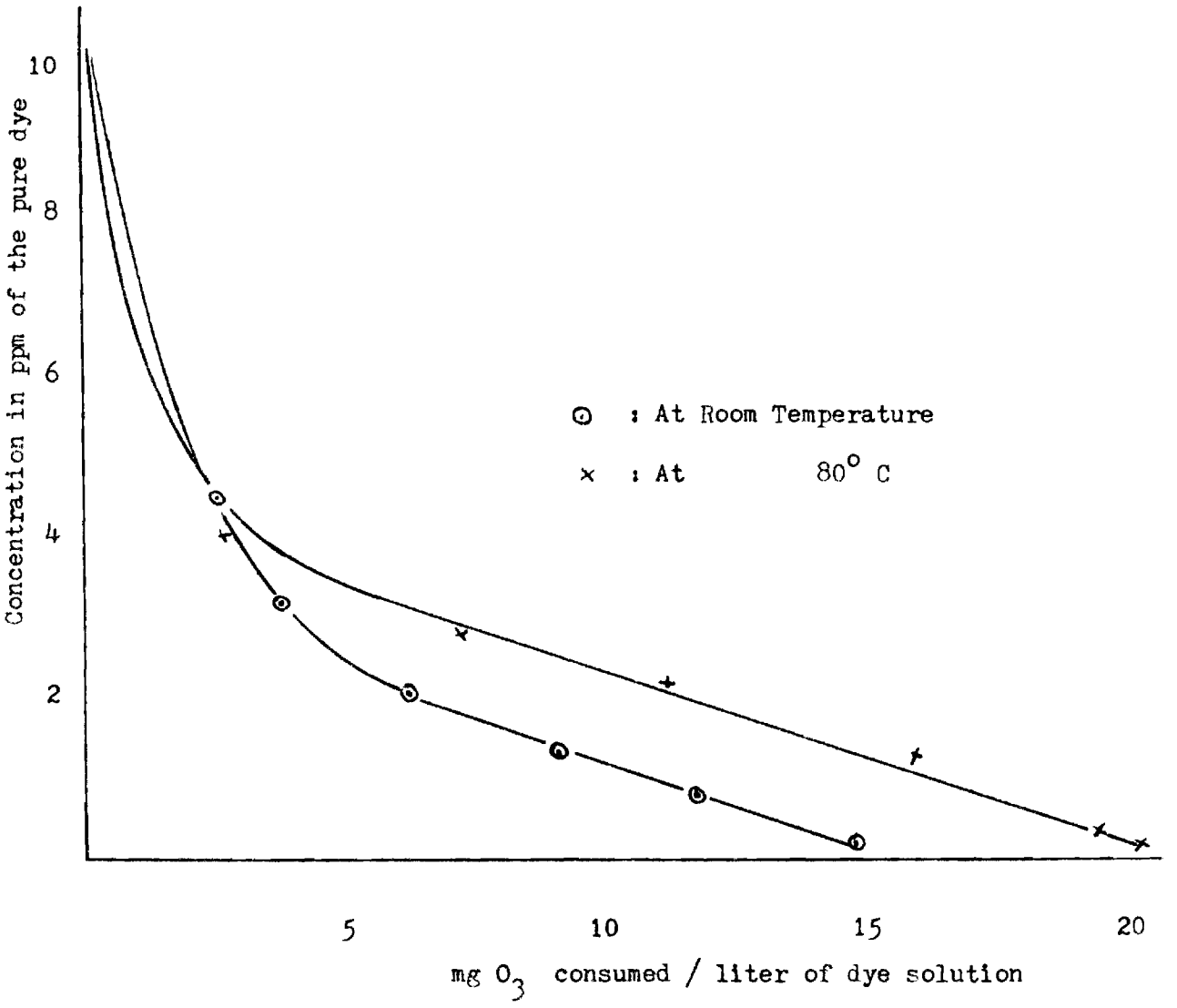


Figure 3. Decolorization of Acid Blue 40 by Ozone

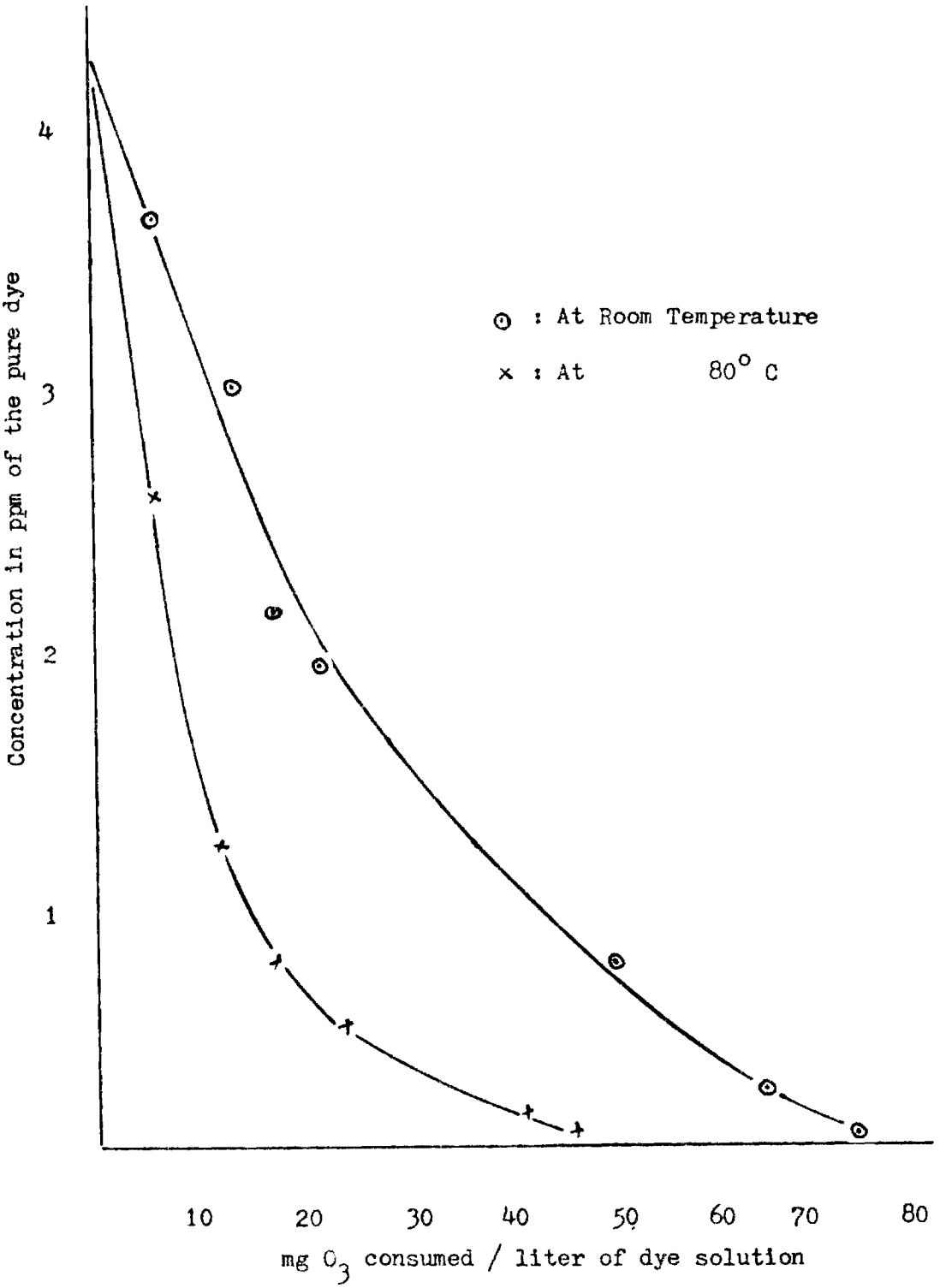


Figure 4. Decolorization of Disperse Blue 7 by Ozone

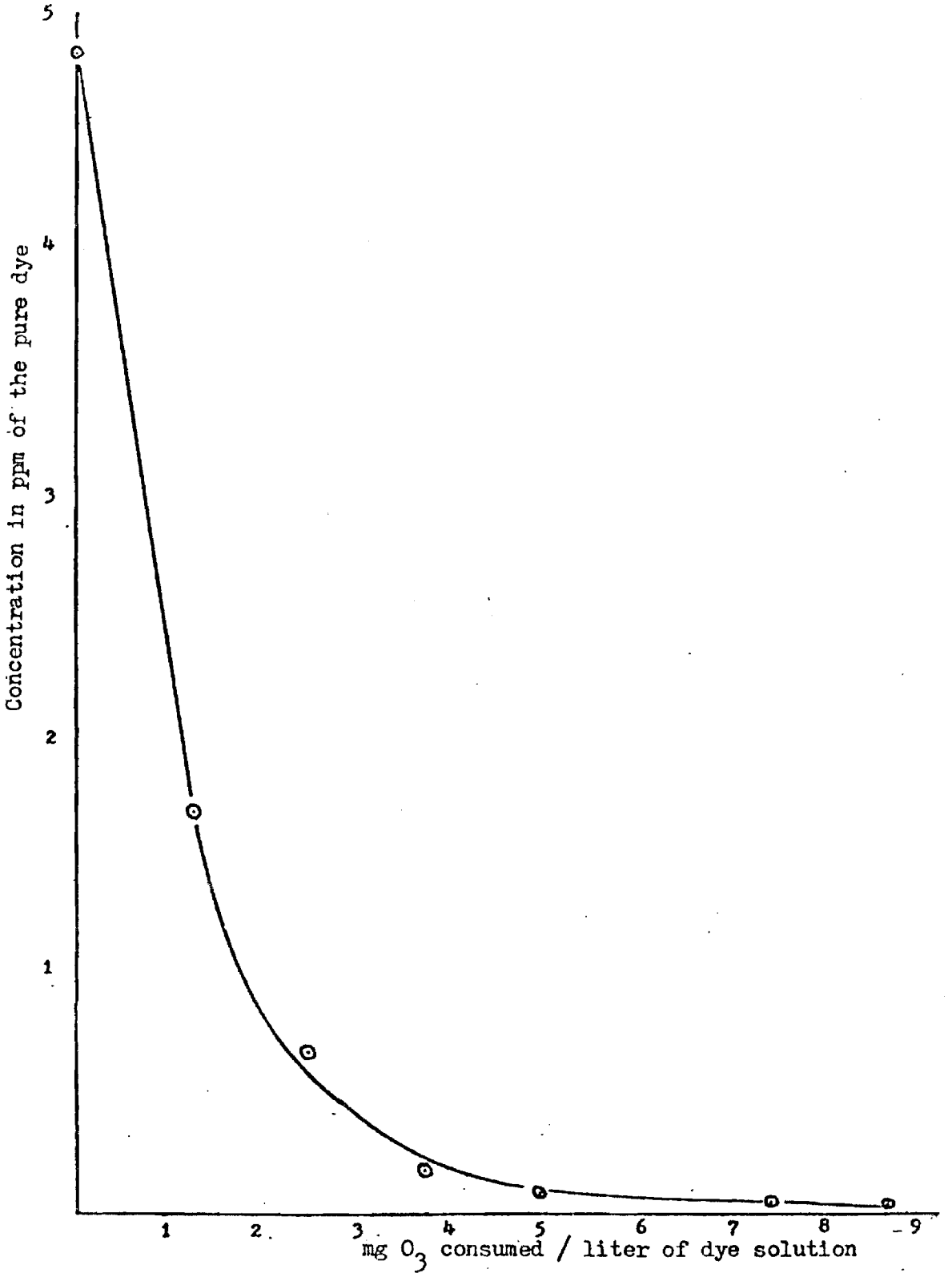


Figure 5. Decolorization of Basic Yellow 11 by Ozone

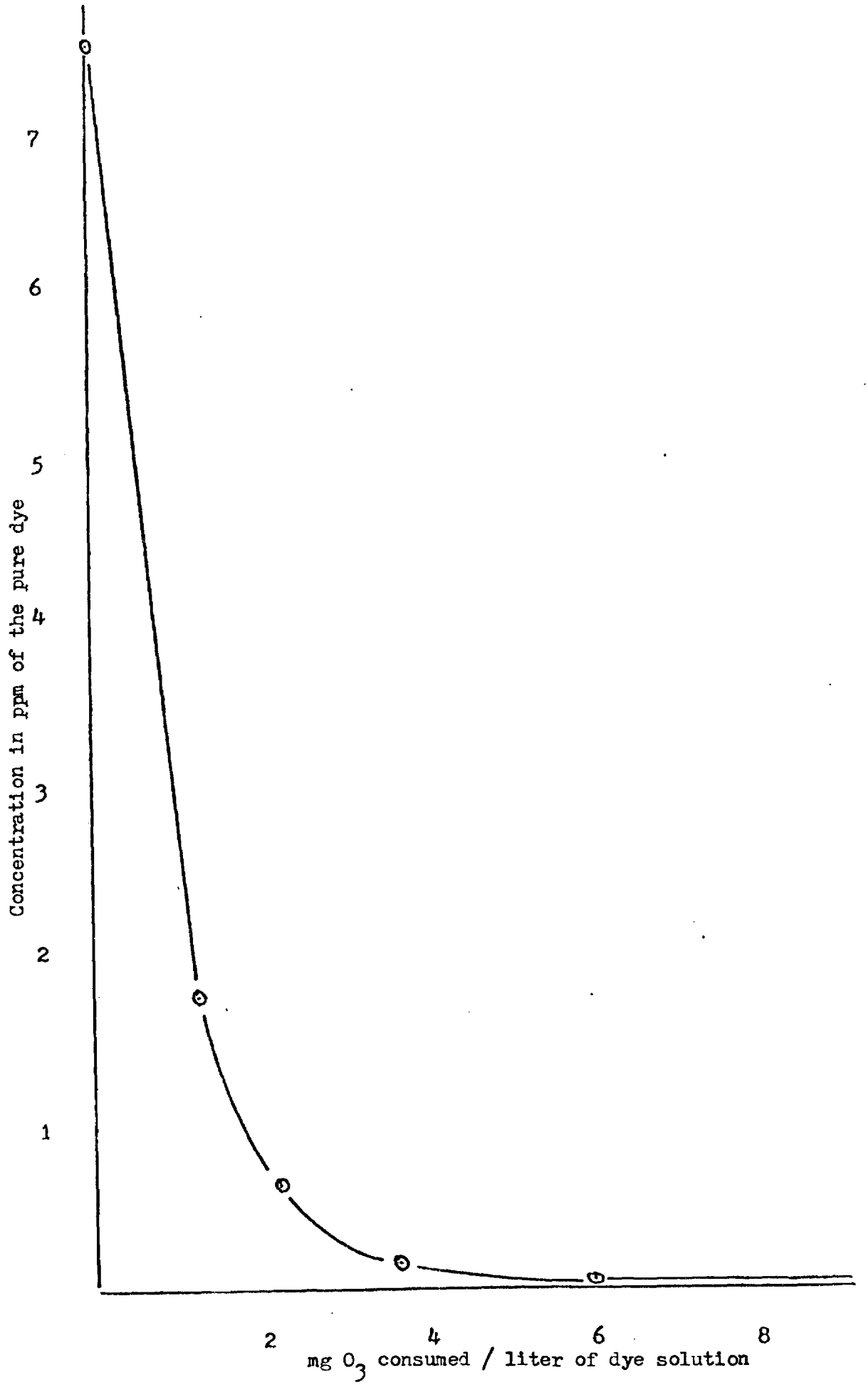


Figure 6. Decolorization of Acid Red 151 by Ozone

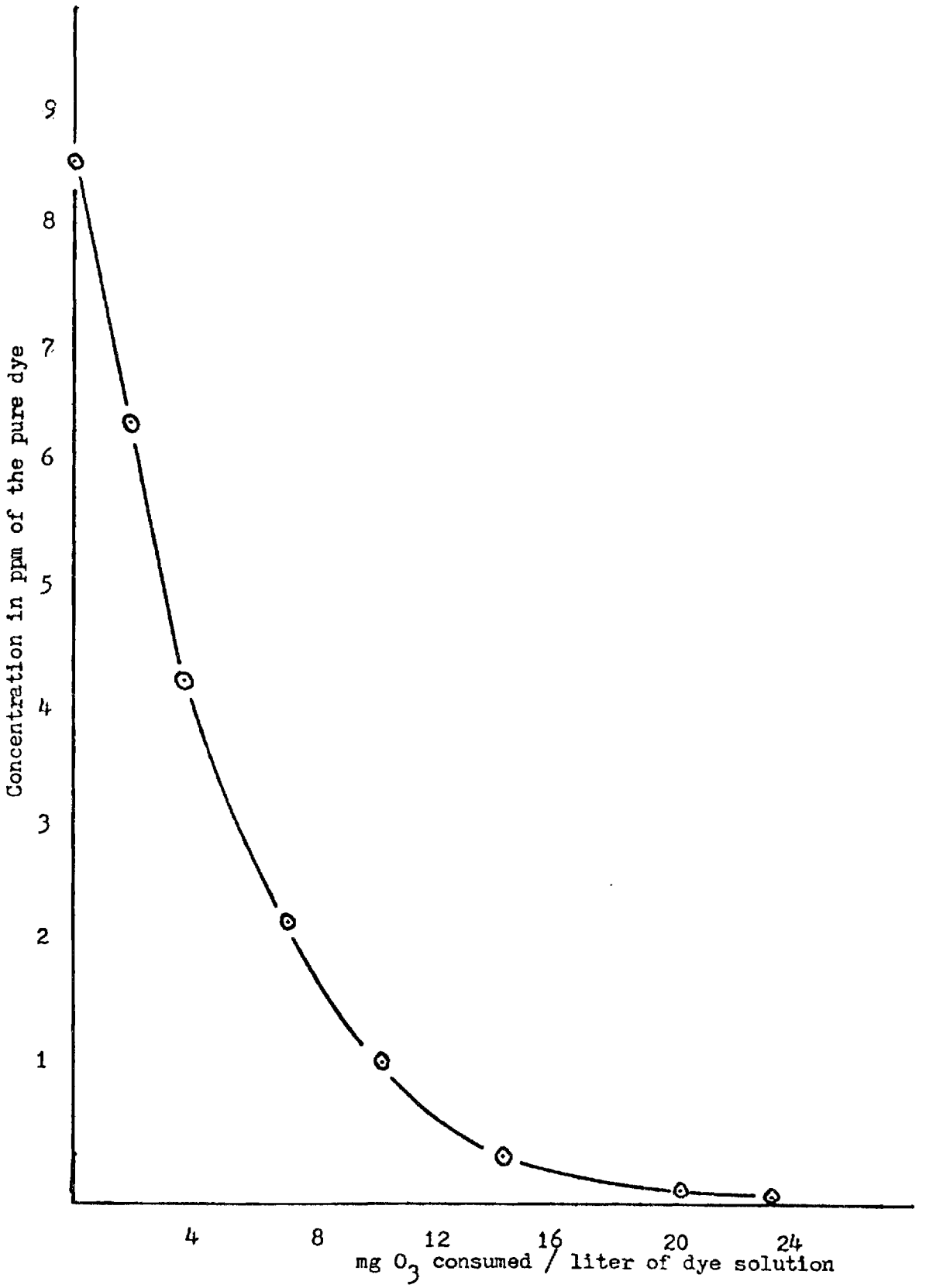


Figure 7. Decolorization of Acid Yellow 19 by Ozone

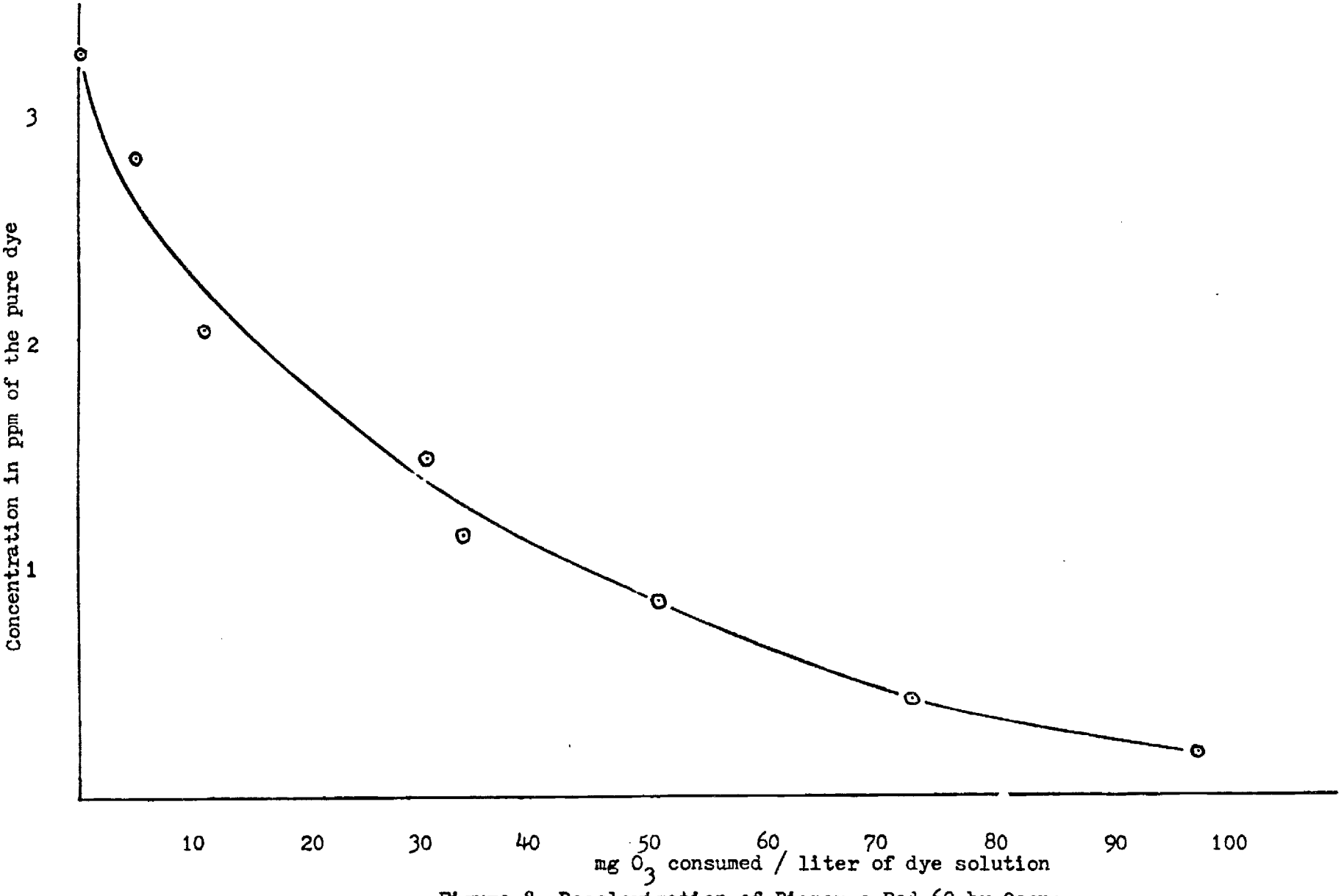


Figure 8. Decolorization of Disperse Red 60 by Ozone

to decolorize acid and basic dyes. Disperse dyes require much larger quantities of ozone.

One of the attractive features of decoloration and reuse of dyeing wastewater is the possibility of recycling hot water in the system. Hot water recycle could substantially reduce the quantity of energy required in textile dyeing operations. Recovery of hot water in the recycle system will require decoloration with selected oxidants at elevated temperatures.

Ozone decoloration experiments have been carried out on several dyes at 80°C. This temperature was selected as representative of the temperature expected in a treatment tank when dyebaths at the boil are discharged to the system. Results of the high temperature ozone treatments are shown in Figures 2, 3 and 4 for Disperse Yellow 42, Acid Blue 40, and Disperse Blue 7.

Results of the high temperature decoloration experiments are very interesting in that both disperse dyes are decolorized more efficiently by ozone at 80°C than 25°C. The acid dye is decolorized more efficiently at 25°C. It is probable that the greater solubility of disperse dyes at 80°C is responsible for the increased efficiency of decoloration. Acid dyes, on the other hand, are actually in solution in the dyebath. The decreased solubility of ozone at higher temperature probably reduces the efficiency of decoloration for acid dyes.

The change in ozone required for acid dye decoloration increased approximately 30% at elevated temperatures. The change in required ozone for disperse dye decoloration was more dramatic, an approximately 40% to 70% reduction. This reduction for disperse dye decoloration is especially significant since disperse dyes require much larger quantities of ozone

for decoloration. The reduced ozone demand at the higher temperature should have a very favorable impact on the economics of the decoloration process.

D. The Effect of Ozone on Dyeing Auxiliary Chemicals

In addition to dyes, spent dyebaths will have appreciable quantities of auxiliary chemicals added to control the dyeing process. These chemicals will also react with ozone and the rate of reaction compared to ozone reaction with dyes will be an important consideration in the economic evaluation of ozone decoloration and dyebath reuse.

Two typical auxiliary chemicals were selected for initial study. Avitone T (duPont) is an anionic surfactant used as a dispersing agent for disperse dyes. Chemcogen 12LD (Chemical Processing of Georgia) is a typical anionic type levelling agent used in acid dyeing of nylon carpets. Results of the exposure of these two auxiliary chemicals to ozone at room temperature ($25^{o}C$) are shown in Figure 9. The quantities of the surfactants in the control and ozone treated solutions were determined using the methylene blue active substances procedure (Standard Methods for Examination of Water and Wastewater).

Results of the study of effects of ozone on auxiliary chemicals were encouraging since they indicate that these types of compounds react more slowly with ozone than the dyes. They should, therefore, have a low ozone demand during dye decoloration and substantial quantities of the auxiliary chemicals should be recyclable in the process.

E. Dyeing Experiments

Nylon carpet samples dyed with a mixture of acid and basic dyes were selected for initial studies.

A large piece of nylon carpet was prescoured to remove fiber lubricants, identification tints, etc. A 50 gram sample of the carpet was placed in a 5-liter beaker and 1.5 liters of water (liquor ratio of 30:1) were added. A leveling agent, Chemcogen 12LD (0.5 grams or 1% owf), and pH control agent, monosodium phosphate (0.5 g or 11% owf) were added. A few drops of an antifoaming agent, Nofome HS (Chem-Mark, Inc.) were also added. The following dyes were used:

Acid Red	0.0115 g	(0.023% owf)
Acid Blue 40	0.0160 g	(0.0327% owf)
Basic Yellow 11	0.1750 g	(0.35% owf)

The temperature was raised to 100°C at 2°C per minute and held at 100°C for fifteen (15) minutes. Acetic acid was added to adjust the pH to 4.5 and the dyeing continued for thirty (30) additional minutes. The carpet was removed from the beaker and rinsed and afterscoured.

The residual dyebath of 1050 ml (after losses due to evaporation and water removed with the carpet) was then exposed to ozone to decolorize the residual dyes. The quantities of ozone required are given in Table 2. The dyebath was used for five (5) consecutive dyeings before being discarded. As indicated in Table 2, the quantity of ozone actually required for dyebath decoloration was very close to the amount calculated from the residual dye concentration and the ozone dye decoloration curves previously obtained.

F. Polyester Carpet Dyeings

Polyester carpet samples have been dyed with disperse dyes in a manner similar to the nylon carpet dyeings described previously. A

Table 2. Decolorization of Waste Dyebaths of Nylon Carpet Dyeings

No of Dyeing	Absorbance after Dyeing			Conc. of Pure Dye ppm			Decolorization %			Calculated O_3	Actual O_3
	410nm	511nm	620 nm	Red	Blue	Yellow	Red	Blue	Yellow	Required mg/l	consumed mg/l
1	.1271	.0115	.0098	.12	.62	1.31	100	100	98	3.3	3.9
2	.1831	.0063	.0018	.07	.14	1.95	100	100	99	3.4	4.2
3	.2880	.0060	.0016	.06	.14	3.08	100	100	100	5.6	6.0
4	.3229	.0062	.0022	.06	.18	3.45	100	100	100	6.3	7.4
5	.3348	.0052	.0021	.05	.18	3.58					

large piece of polyester carpet was prescoured to remove fiber lubricants, identification tints, etc. A 50 gram sample of the carpet was placed in a 5-liter beaker and 1.5 liters of water (liquor ratio of 30:1) were added. A dye dispersing agent, Avitone T (0.5 grams or 1% owf), a pH control agent, monosodium phosphate (1.0 gram or 20% owf) and a few drops of an antifoaming agent, Nofome HS, were added.

The following dyes were used:

Disperse Yellow 42	0.170% owf	or	0.085 grams
Disperse Red 60	0.020% owf	or	0.010 grams
Disperse Blue 7	0.030% owf	or	0.015 grams

The pH was adjusted to 5.0 with acetic acid and a dye carrier, Carolid L-65, (10% owf or 5 grams) was added. The temperature was raised to 100^{o}C and maintained for 1 hour. The carpet sample was then removed from the beaker, rinsed with warm water, afterscoured, and dried at 120^{o}F for 1 hour.

The used dyebath (1050 ml) was then exposed to ozone to decolorize the residual dyes. The bath was then reconstituted to its original volume and used for the next dyeing. Five dyeings were carried out in the same bath.

Ozone consumption for decolorization of the spent dyebaths are shown in Table 3. As noted for the nylon carpet dyeings, the actual ozone requirements were very similar to the calculated requirements based on dye decolorization experiments carried out earlier.

G. Evaluation of Samples Dyed in Recycled Dyebaths

The five samples of nylon carpet dyed consecutively in the same dyebath by decolorizing with ozone and reuse of the bath have been

Table 3.

Decolorization of Waste Dyebaths of Polyester Carpet Dyeings

NO. OF DYEING	ABSORBANCE AFTER DYEING			COMM. DYE CONCENTR. ppm			DECOLORIZATION %			Calculated O_3 Required mg/l	Actual O_3 Consumed mg/l
	415.5nm	515.5nm	605nm	Red	Blue	Yellow	Red	Blue	Yellow		
1	.0341	.0051	.0170	1.38	5.59	26.25	100	100	96	379.0	414.6
2	.0270	.0062	.0134	3.04	4.39	20.69	100	100	94	300.5	332.7
3	.0306	.0077	.0131	4.71	4.27	23.52	100	100	95	347.1	380.2
4	.0264	.0065	.0176	2.42	5.77	19.96	100	100	92	288.0	323.2
5	.0272	.0054	.0119	2.47	3.90	20.96	100	100	95	302.9	330.1

evaluated for color reproducibility, stability of the color to light exposure (lightfastness), colorfastness to water exposure, and colorfastness to abrasion (crockfastness). Standard exposure conditions and evaluation procedures were used to assess the quality of the dyeings in recycled baths.

1. Color Reproducibility

Instrumental measurements of color were used to assess the between sample color variation in the dyeings. A Diano LSCE Automate color measuring instrument was used for color measurement.

In color measurement on the samples of nylon carpet dyed with acid and basic dyes it was necessary to make measurements on yarn removed from the carpet. This was done because the differentially dyeable nylon fibers gave different colors when dyed with acid and basic dyes and the differently dyed areas in the carpet were not large enough for direct measurement on the Automate. The individual yarns were removed and wrapped loosely and uniformly around strong rectangular white paper in such a way that all the surface was covered by the loose yarns. For each sample six measurements were obtained, three in a horizontal position and three in a vertical position of the yarns. The average of these six measurements (expressed as the tristimulus values, X, Y, and Z) was taken as the tristimulus values for each sample. The first conventionally dyed carpet was taken as the standard.

Color differences between the first dyeing (in a fresh bath) and the 4 subsequent dyeings (in the recycled bath) were calculated using the Friele-MacAdam-Chickering equation (FMC-II). In this system, 1 unit of color difference is a just perceptible color difference to the average

observer. Results of the color difference calculation for the regular nylon yarn and the nylon yarn that dyes with the basic dye and the polyester carpet samples are shown in Table 4.

The color difference values, DE, in Table 4 are of the order of 2 or 3 FMC-II units in the nylon samples. This agrees quite favorably with typical color differences encountered in carpet production. In general, color differences as large as 5 FMC-II units are considered acceptable matches in carpet dyeing. Thus, all of the nylon dyeings in recycled baths were within acceptable limits for first quality carpet production.

Somewhat larger differences of the order of 5 or 6 MacAdam units are observed for the polyester dyeings in recycled baths. Apparently during the decolorization of waste dyebaths containing disperse dyes, oxidation by-products are formed and accumulate which can oxidize a portion of the dyes added for the subsequent dyeing. The color difference increases for each dyeing run if the decolorized dyebath is reused without being reduced (run 2-5).

In order to correct this problem a sixth run was made in the spent dyebath by adding a small amount of a reductant, $N_{a2}\ S_2\ O_3$, (sodium hydrosulfite is a common reductant used in textile operations) prior to the added dye and sample six is well within acceptable color difference limits. This procedure would probably be required in production use for polyester dyeings.

2. Crockfastness

Colorfastness to rubbing (crocking) was evaluated by the American Association of Textile Chemists and Colorists (AATCC) Test Method Number 8.

Table 4. Color Data on Reproducibility from Run to Run

Sample			Tristimulus Values							
			X	Y	Z	DCRG	DCYB	DC	DL	DE
Acid Dyed Nylon	Std	No 1	31.91	29.10	29.05	-	-	-	-	-
(Purple)	Sample	No 2	31.96	29.18	30.06	-.187	-.683	3.340	.165	3.340
		No 3	31.46	30.23	29.86	-.145	-.941	3.653	-1.007	3.789
		No 4	31.76	29.31	29.14	-.295	.035	3.878	.293	3.889
		No 5	31.04	28.09	29.00	.033	-.666	2.245	-2.034	3.029
Basic Dyed Nylon	Std	No 1	56.13	58.82	14.98	-	-	-	-	-
(Yellow)	Sample	No 2	57.46	60.54	14.45	-.086	.697	2.802	2.185	3.553
		No 3	56.97	59.56	14.55	.217	.457	2.560	1.008	2.751
		No 4	56.53	59.13	14.00	.272	.779	3.805	.432	3.830
		No 5	56.60	58.96	14.42	.381	.448	3.676	.270	3.686
Polyester	Std	No 1	30.17	31.25	21.69	-	-	-	-	-
	Sample	No 2	30.13	30.94	21.87	.148	-.226	2.219	-.541	2.284
		No 3	30.65	31.56	22.59	.034	-.483	2.011	.711	2.011
		No 4	31.05	31.90	23.72	-.061	-1.127	4.647	1.451	4.869
		No 5	30.71	31.04	22.60	.440	-.706	6.424	-.159	6.426
		No 6	30.24	31.29	21.79	.016	-.050	0.293	.095	0.308

Carpet samples were cut oblique to the warp and weft directions of the carpet backing and subjected to 20 cycles on a standard Crockmeter. The evaluation of color transfer was conducted by means of the AATCC Chromatic Transference Scale. Results of the colorfastness to crocking test are shown in Table 5. It is clear that the samples dyed in recycled baths are identical to the conventional dyeing run.

3. Colorfastness to Water

The method for testing fastness to water was AATCC Test Method 107. The test was carried out as per specifications in the AATCC Technical Manual, except for the fact that multifiber Test Fabric No. 10 (containing spun acetate, bleached cotton, spun nylon 66, spun Dacron 54, spun Orlon 75, worsted wool) was used instead of multifiber Fabric No. 1 (containing spun acetate, bleached cotton, spun nylon 66, spun silk, spun biscose, worsted wool). Plexiglass plates of specified deminsions were used between specimens. The evaluation of fastness was done by means of the AATCC Gray Scale for Staining.

Results of the colorfastness to water test are shown in Table 6. Again, the samples dyed in recycled baths show similar behavior to conventional dyeings.

4. Colorfastness to Light

Lightfastness was evaluated by AATCC Test Method 16F, which is the testing of colorfastness to continuous light from a water-cooled xenon-arc lamp. The samples were exposed to the light source for 20, 40, 50, 80, 100, and 120 hours. The light fastness was evaluated by comparing the differences between exposed and unexposed strips of the sample with the AATCC Gray Scale for Color Change.

Table 5. Evaluation of Fastness to Dry Crock

Carpet	Run No	Ratings
Nylon	1	5
(Purple)	2	5
	3	5
	4	5
	5	5
Nylon	1	5
(Yellow)	2	5
	3	5
	4	5
	5	5
Polyester	1	5
	2	5
	3	5
	4	5
	5	5
	6	5

Table 6. Evaluation of Fastness to Water

Carpet	Run No	Ratings
Nylon	1	4
	2	4
	3	4-5
	4	4-5
	5	4-5
Polyester	1	5
	2	5
	3	5
	4	5
	5	5
	6	5

Results of colorfastness to light tests are shown in Table 7. The conventionally dyed sample and samples dyed in recycled baths show similar lightfastness properties.

III. CONCLUSIONS

Results of the first year's effort on the project have led to a number of important conclusions about decolorization and reuse of dyeing wastewater.

1. Acid/basic dyes can be readily destroyed by treatment with ozone. Disperse dyes can also be destroyed but require a larger quantity of ozone.
2. Textile auxiliaries are not as rapidly destroyed as dyes by ozone. It should be possible, therefore, to destroy the color and reuse both the water and a substantial quantity of auxiliary chemicals.
3. Nylon carpet can be dyed in decycled baths that have been decolorized by ozone. Carpets dyed in recycled baths are of acceptable commercial quality.
4. Polyester carpet can be dyed acceptable in ozone decolorized baths if the bath is treated with a reductant prior to reuse.

IV. FUTURE WORK

Work during the second year on this project will be directed toward evaluating excited "singlet oxygen" spines produced by a short wavelength UV light source as a means of decolorizing dyebaths. Work will continue on mechanisms of ozone degradation of dyes and on economic evaluation of the decoloration and reuse systems.

Table 7. Evaluation of Light Fastness

Carpet	Run No	Hours of Exposure					
		20	40	60	80	100	120
Nylon	1	4-5	4	3	1-2	1	1
(Purple)	2	5	3-4	3	1-2	1	1
	3	5	4	3	1-2	1	1
	4	5	4	3-4	1-2	1	1
	5	5	4	3-4	1-2	1	1
Nylon	1	5	4-5	4	3-4	3-4	3
(Yellow)	2	5	4-5	4-5	4	3-4	3
	3	5	5	4-5	4	4	3-4
	4	5	4-5	4-5	4-5	4	3-4
	5	5	5	4-5	4	3-4	3-4
Polyester	1	5	5	4-5	4-5	4-5	4
	2	5	5	5	4-5	4-5	4
	3	5	5	5	4-5	4-5	4-5
	4	5	5	5	4-5	4-5	4
	5	5	5	4-5	4-5	4-5	4
	6	5	5	5	4-5	4-5	4

REUSE OF TEXTILE DYEING WASTEWATER

Quarterly Progress Report #5

September 1, 1979 - November 30, 1979

OWRT Grant No. 14-34-0001-8813

Research Project E-27-673

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia

December 10, 1979

I. INTRODUCTION

Major effort this quarter has been directed toward development of equipment and establishment of experimental procedures for decolorization of dyebaths by "singlet oxygen". This excited state of oxygen can be produced by short wavelength UV lamps and may be attractive economically for decolorization of dyebaths.

II. EQUIPMENT FOR "SINGLET OXYGEN" DECOLORIZATION.

Two short wavelength denterinm lamps have been obtained from Photozone Inc., Chicago, Illinois. These lamps have been used as a replacement for chlorine containing compounds in swimming pool disinfection. The active species produced by the short wavelength radiation from these lamps is believed to be "singlet oxygen". This excited oxygen species is known to react rapidly with carbon to carbon double bonds and should be effective in destruction of the color of dye molecules.

At least two different modes of operation are possible with these lamps in decolorization of dyeing wastewater. Air may be passed over the lamp and the excited oxygen produced bubbled through the spent dyebath. In the second mode, the spent dyebath with air dissolved in the bath is pumped through a chamber surrounding the lamp. In this mode the dye is exposed to both the low wavelength UV light and excited "singlet oxygen".

The quantity of active oxygen species (analyzed as ozone by the Standard Methods procedure) produces as a function of time is given in Figure 1.

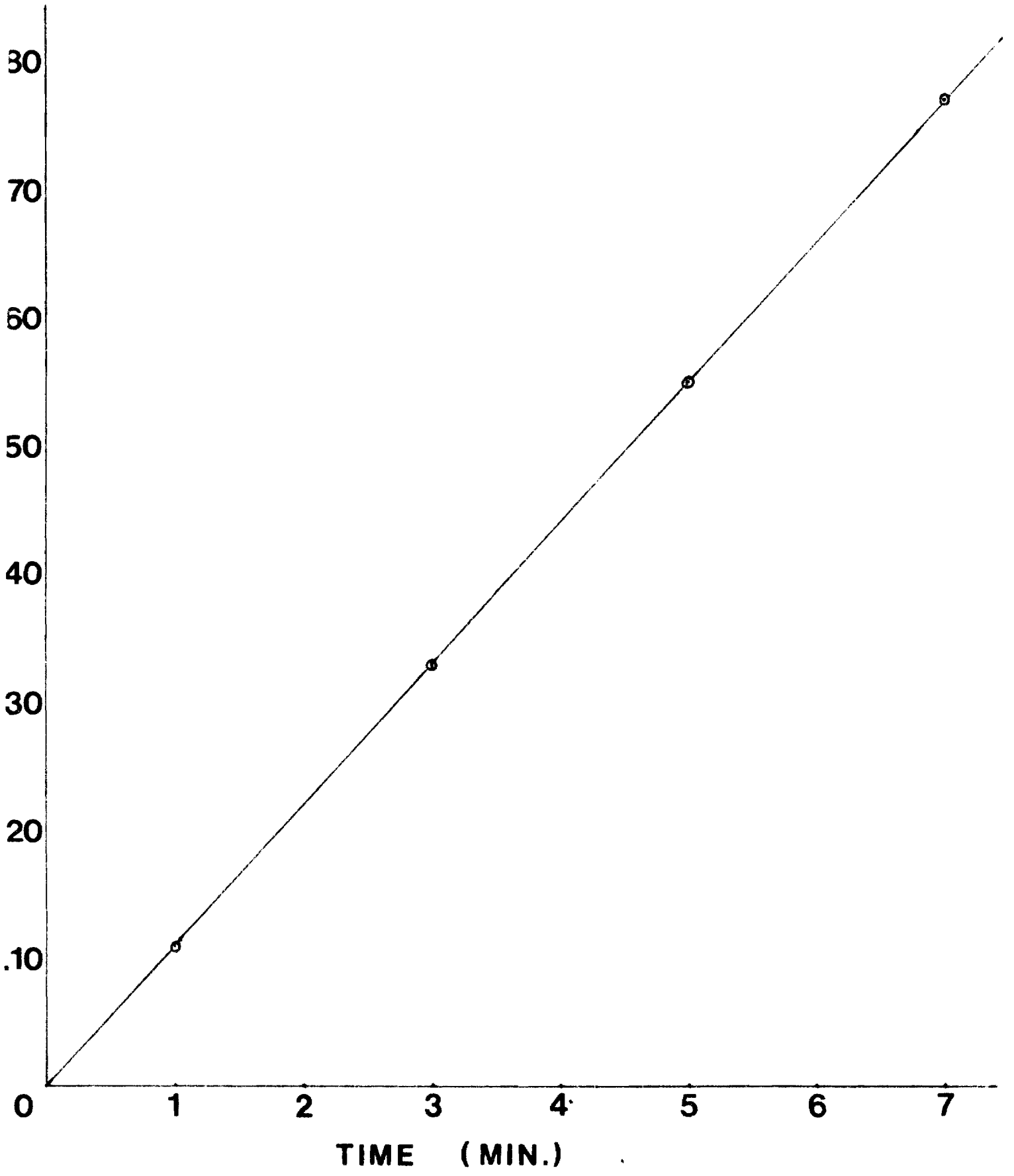


FIGURE I - - Active Oxygen Species Produced by a Photozone Lamp

III. DYE DEGRADATION BY "SINGLET OXYGEN"

The rate of degradation of several dyes by singlet oxygen have been determined by exposure of dye solutions directly to the light from a Photozone lamp. The weight of dye remaining in solution (as determined by absorption spectrophotometry) is plotted versus the weight of active oxygen species produced by the lamp in Figure 3, 4, and 5. It is clear that the combination of short wavelength UV light and "singlet oxygen" is effective in decolorization dyes.

IV. FUTURE WORK

Continued studies on singlet oxygen degradation of dyes is planned for next quarter.

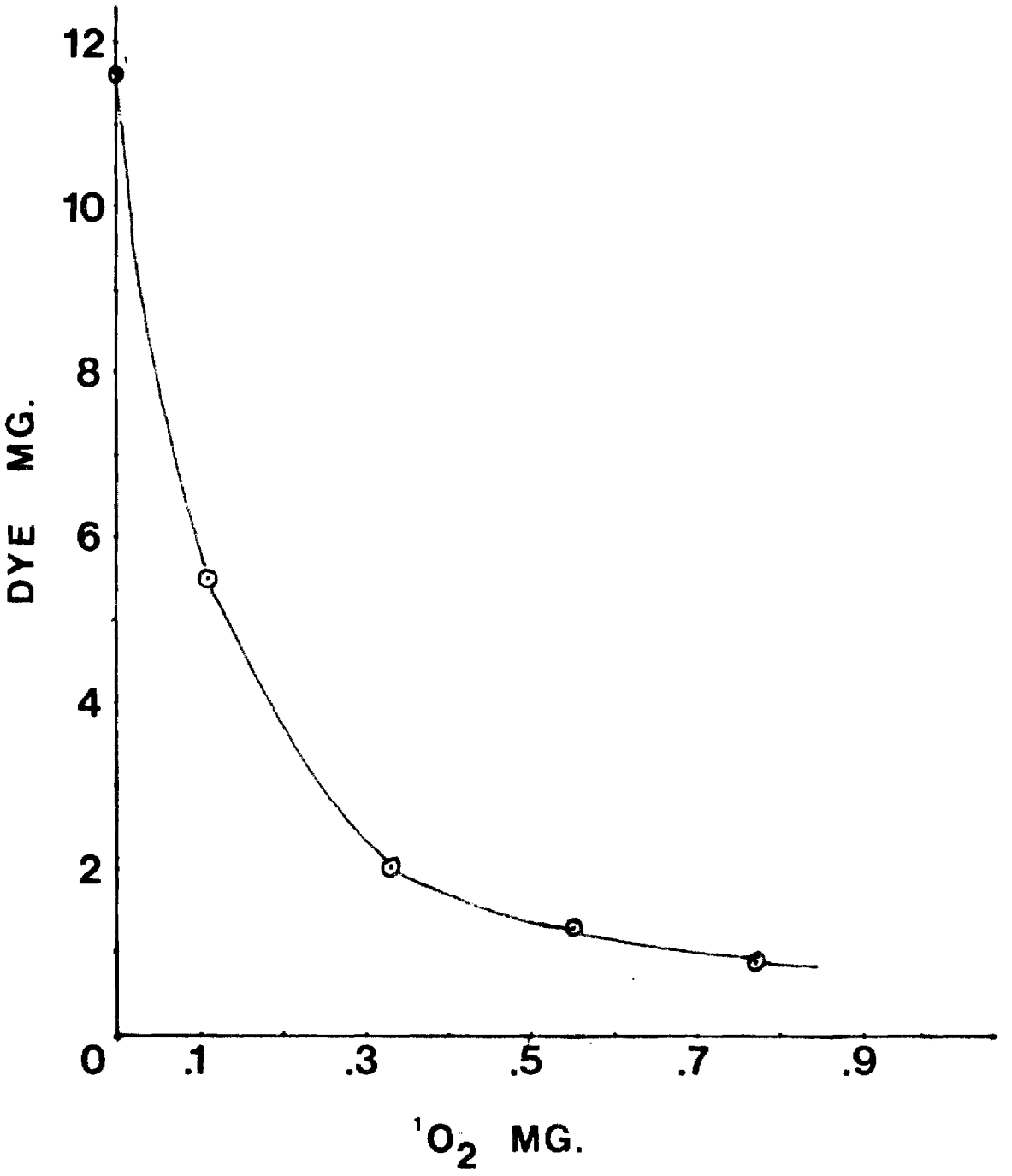


FIGURE 2 -- Destruction of Acid Yellow 19 by Exposure to a Photozone Lamp.

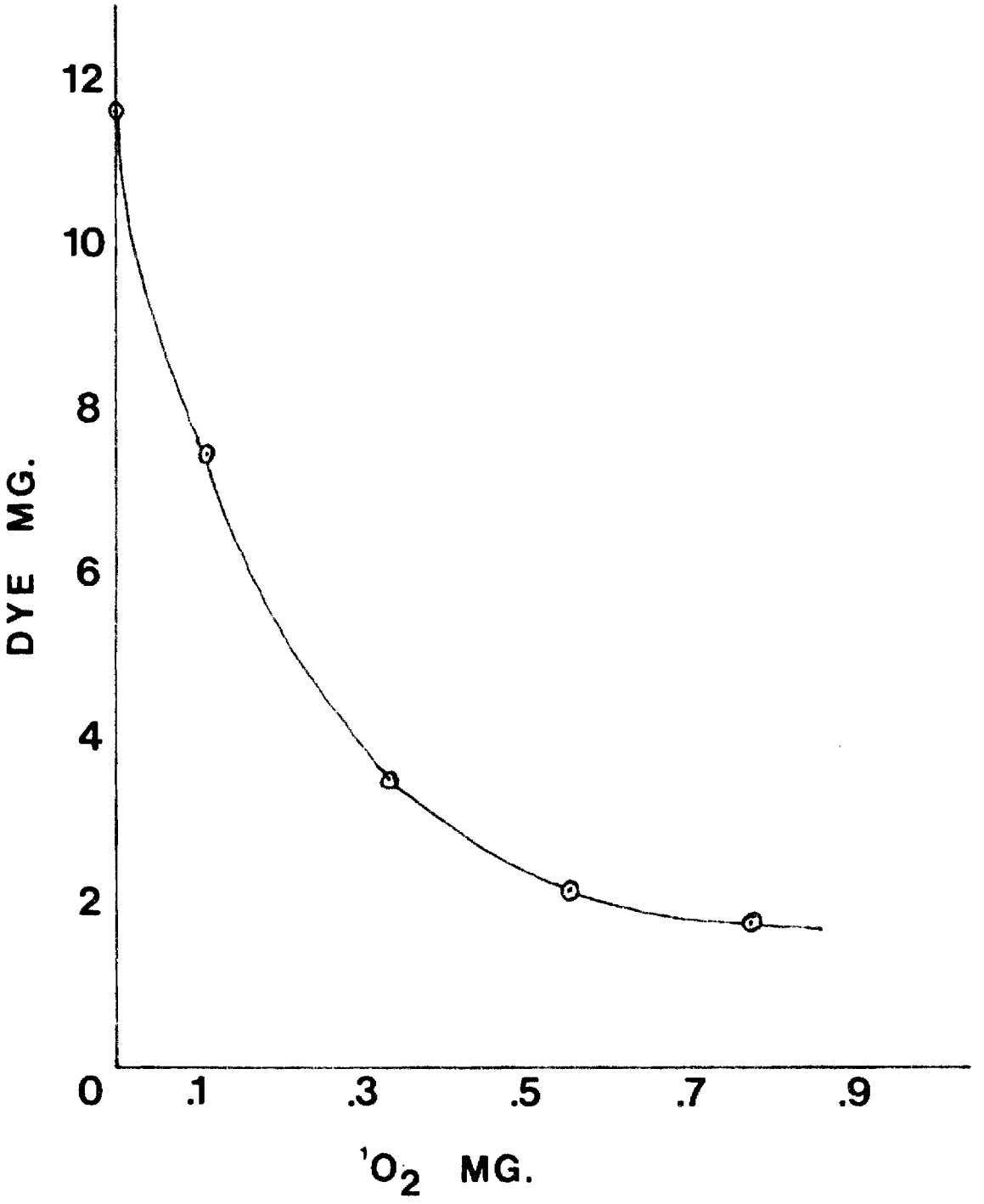


FIGURE 3 -- Destruction of Acid Red 266 by Exposure to a Photozone Lamp.

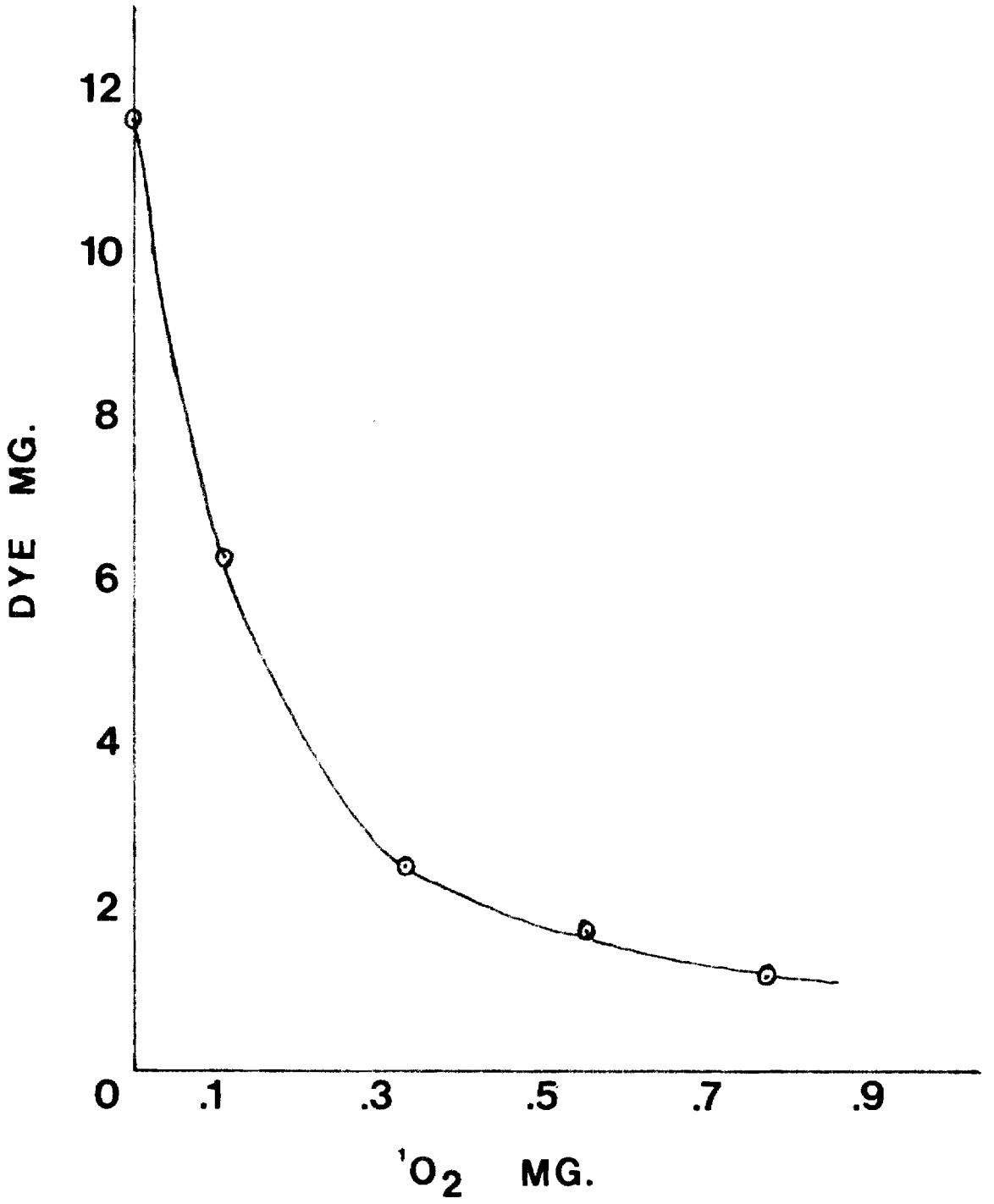


FIGURE 4 -- Destruction of Acid Red 337 by Exposure to a Photozone Lamp.

E-27-673

REUSE OF TEXTILE DYEING WASTEWATER

Quarterly Progress Report #6

December 1, 1979 - February 29, 1980

OWRT Grant No. 14-34-0001-8813

Research Project E-27-673

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia

March 10, 1980

I. Introduction

Efforts have continued this quarter in evaluating excited oxygen species produced by short wavelength ultraviolet lamps for decolorization of dyebaths. Main effort has been directed toward passing oxygen around the lamp and then bubbling the oxygen through solutions of the selected dyes. Similar experiments are reported for air.

II. Production of Excited Oxygen Species

A comparison of the various techniques for production of excited oxygen species is given in Figure 1. The milligrams of excited oxygen species produced measured as ozone by the Standard Methods procedure is plotted vesus time for three different conditions. The largest quantity of ozone per unit time is produced by the standard ozone generator with pure dye oxygen as the feed gas. The short wavelength UV light source with pure oxygen as the feed gas produces somewhat less "ozone" and the UV light source filled with an aerated solution produces very little excited oxygen. The effectiveness of the UV lamp solution method in declorizing dyes must be due primarily to the UV light and not excited oxygen species produced.

III. Dye Degradation with Photozone Lamps

Results of degradation studies on several dyes have been carried out by exposure of air and/or oxygen to the radiation from the Photozone lamp and bubbling the irradiated gas through dye solutions. Results for

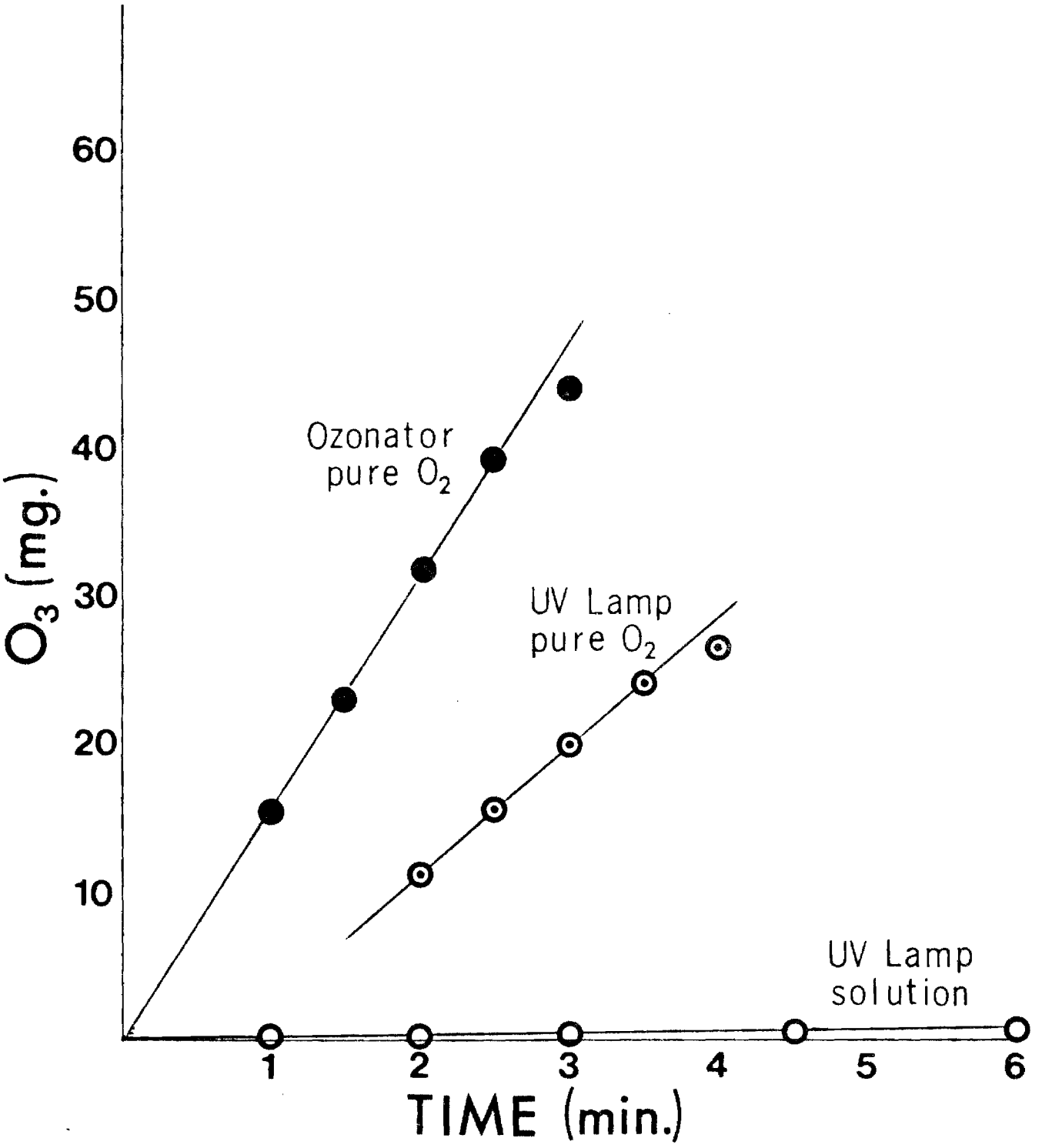


Figure 1. Active Oxygen Species Production

Acid Yellow 19, Acid Blue 25 and Acid Red 266 are shown in Figure 2, 3, and 4 where the weight of dye destroyed in milligrams is plotted versus exposure time. These results suggest that oxygen would probably be required for effective use of the UV radiation system.

IV. Future Work

Singlet oxygen degradation of disperse dyes will be evaluated next quarter.

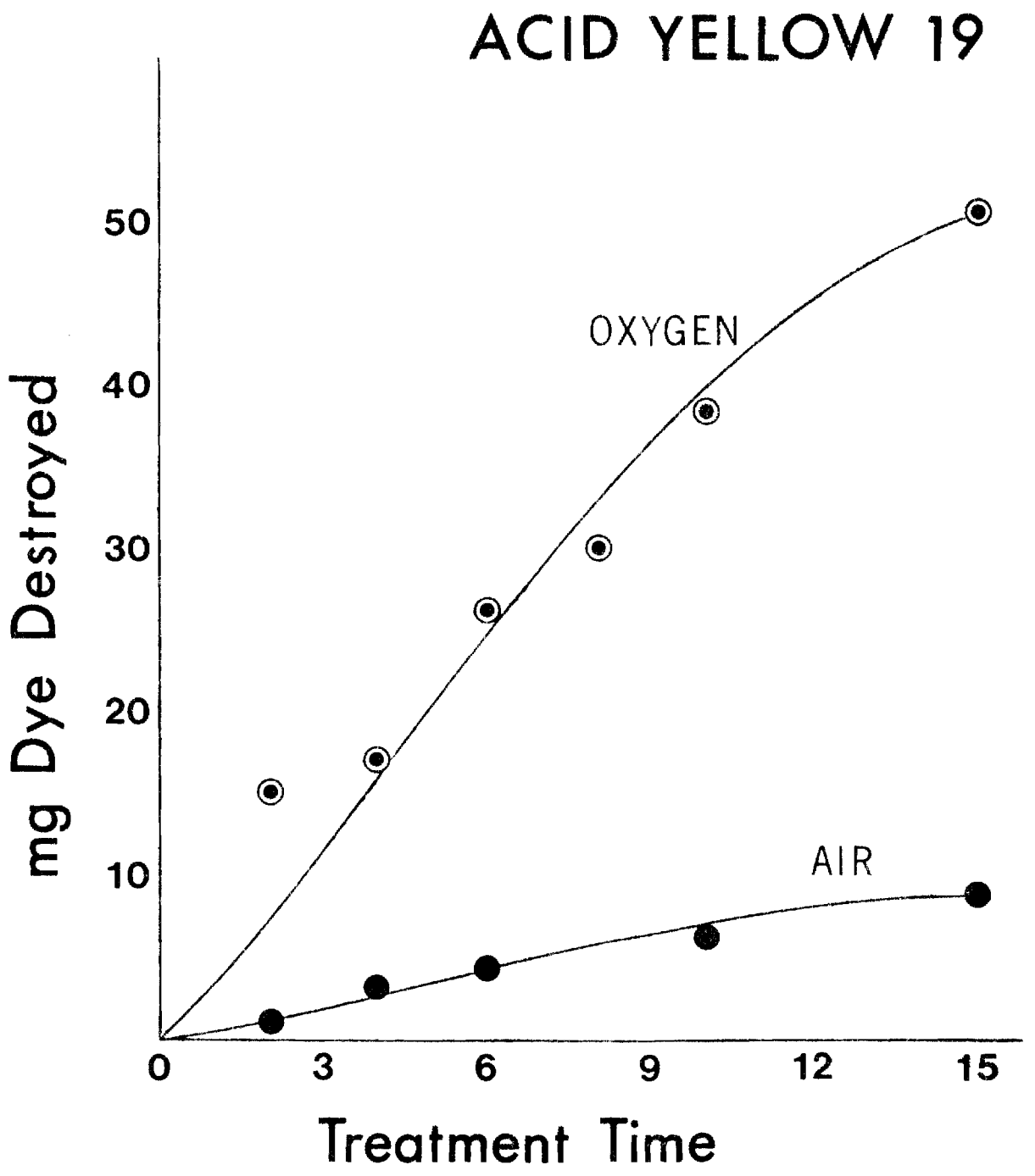


Figure 2. mg Acid Yellow 19 Destroyed with Time

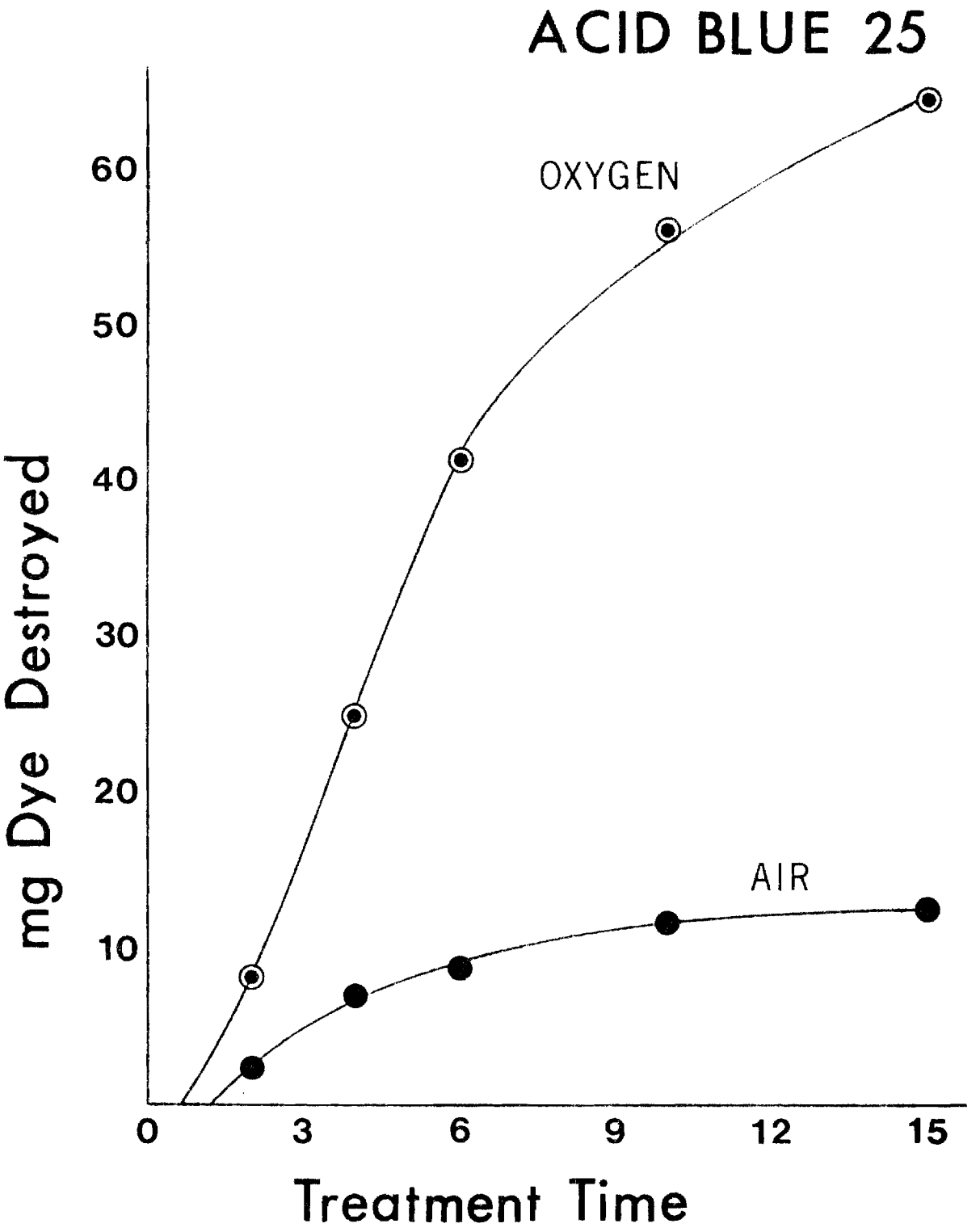


Figure 3. mg Acid Blue 25 Destroyed with Time

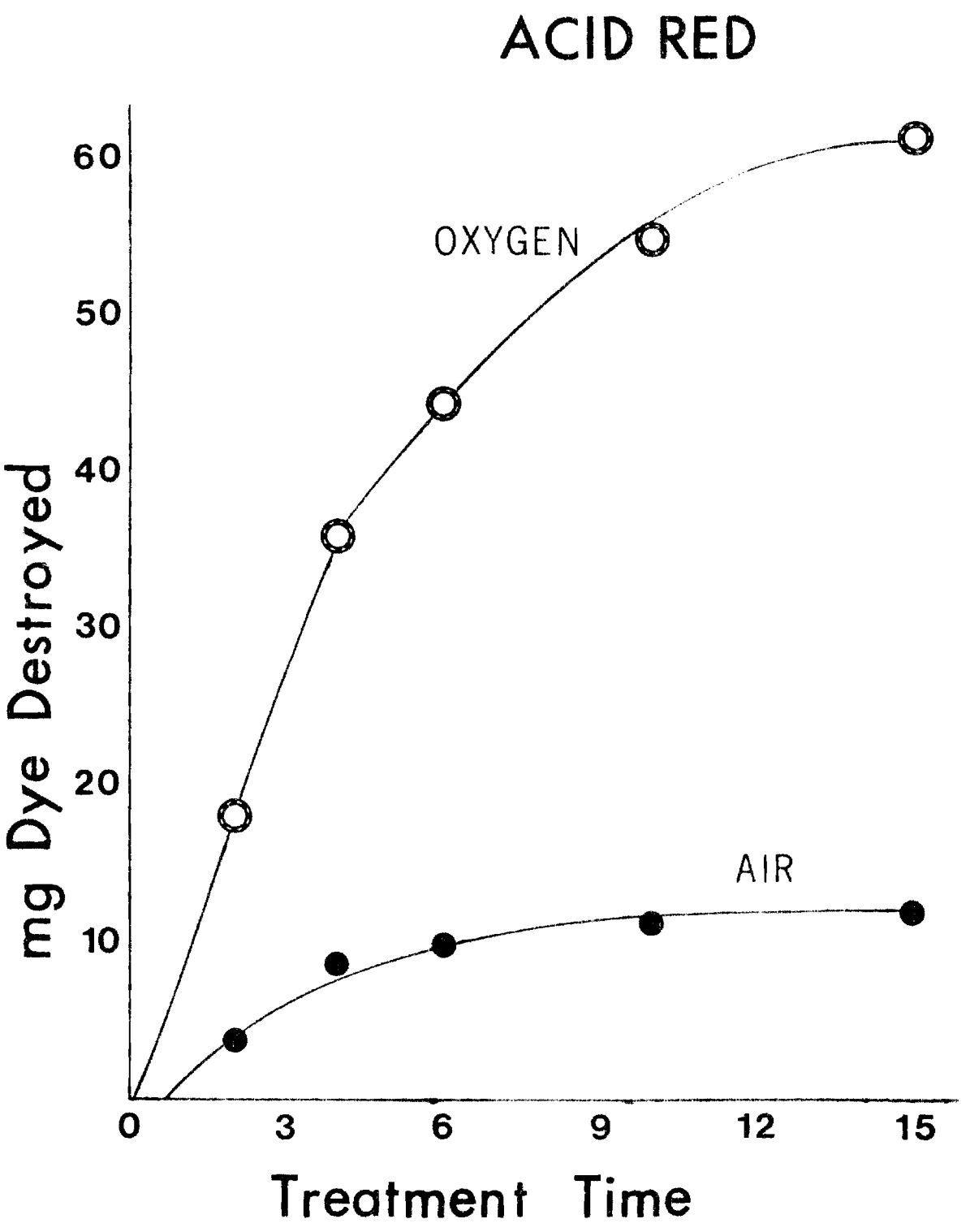


Figure 4. mg Acid Red 266 Destroyed with Time

E-27-673

Reuse of Textile Dyeing Wastewater

Quarterly Progress Report #7
March 1, 1980 - May 30, 1980

OWRT Grant No. 14-34-0001-8813
Research Project E-27-673

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

July 28, 1980

I. INTRODUCTION

Results of degradation studies on several disperse dyes have been carried out in the same manner as in last quarter's report on acid dyes. Dyebath reuses have been attempted on spent dyebaths after degradation using active oxygen species.

II. Disperse Dye Degradation With Photozone Lamp

As in the previous report on acid dye degradation, disperse dye degradation has been studied by flowing either pure oxygen or air through a photozone lamp and then bubbling the irradiated gas through dye solutions. The results are shown in Figures 1, 2 and 3 for Disperse Red 55, Disperse Blue 7 and Disperse Yellow 23. The weight of the dye destroyed in mg is plotted versus time exposed to the irradiated gas. In Figures 1 and 2 the use of oxygen is seen to be more effective than air in dye degradation. In Figure 3, values for UV lamp (air) degradation were not obtainable because of the total insolubility and difficult recovery of the dye.

III. Reuse Dyeings

Reuse dyeings have been carried out successfully using an ultraviolet lamp degraded spent dyebath containing either acid or disperse dyes and common auxiliaries.

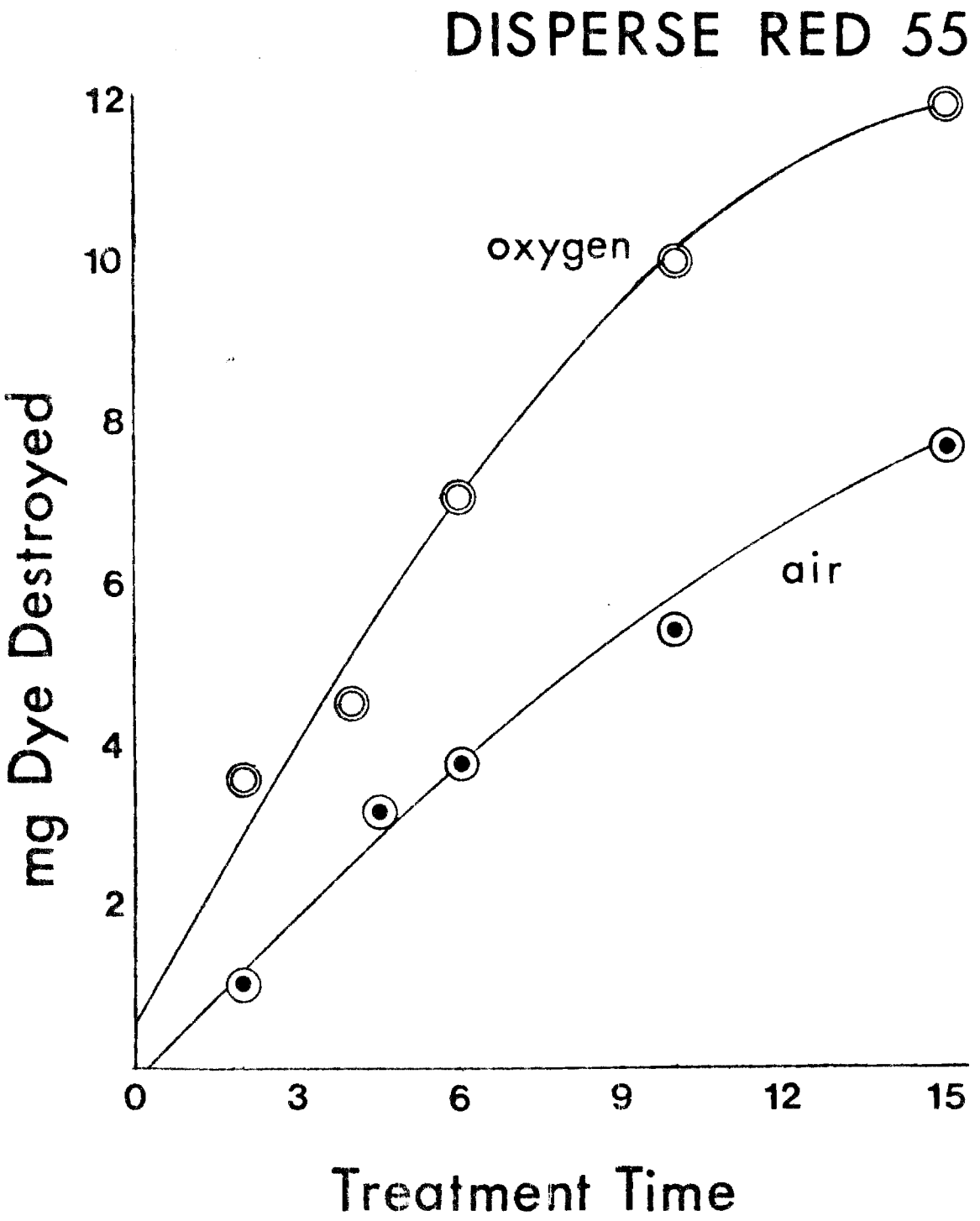


Figure 1. mg Disperse Red 55 Destroyed in Time

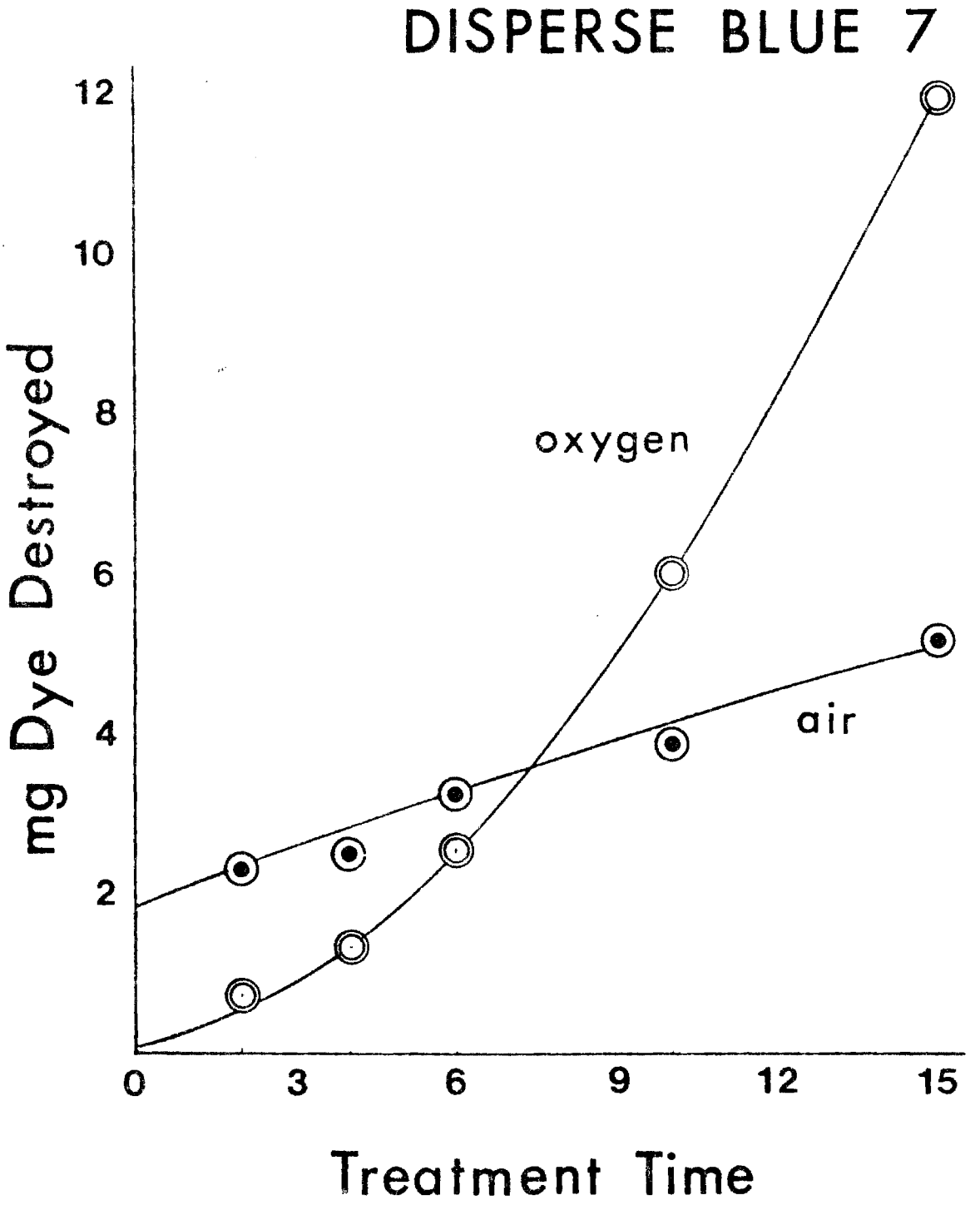


Figure 2. mg Disperse Blue 7 Destroyed in Time

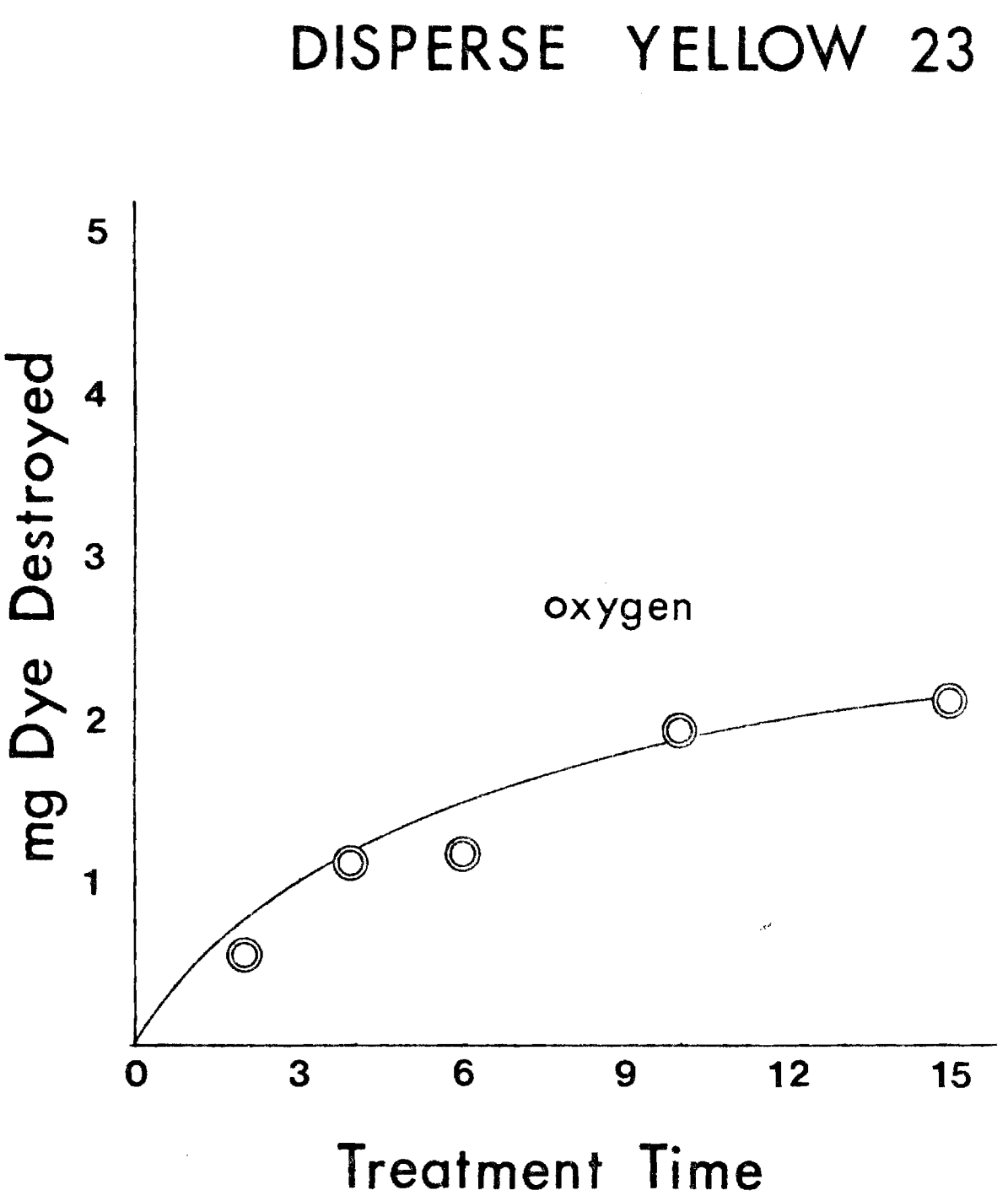


Figure 3. mg Disperse Yellow 23 Destroyed in Time

Four nylon carpet samples were consecutively dyed in one dyebath using disperse dyes. After each dyeing, active oxygen species produced from a photozone lamp were diffused through the bath until no discernible color remained. Color differences measured for each reuse versus the first sample (taken as the standard) remained well within limits that are commercially acceptable, as seen in Table 1.

An acid dyeing sequence of 4 reuses gave similar results using air ozonolysis. The high color difference of 9.2 MacAdam units (Reuse 3) was caused by a weighing error. The other values fall within acceptable limits.

Using the formulation of an actual commercial dyeing, a standard dark brown dyeing was carried out using nylon carpet, followed successfully by two dark brown reuses. For a rigorous test of the active species degradation, a light beige sample was dyed as a third reuse. The color difference between the third reuse and a standard light beige sample was very acceptable, being only 2.4 MacAdam units.

Figure 4 indicates the efficient degradation of absorbing species of an exhausted dyebath. Absorbance is plotted versus nm as the spectrophotometer scanned from 700 to 400 nm. To obtain the degraded sample, air was passed through an ozonater, than bubbled through the dyebath until color could not longer be seen, approximately 30 minutes.

Table 1. Color Difference Data for Reuse Dyeings

Type of Dyeing	Method of Degradation	Method in Same Bath	Sequence of dyeing Sample	Color Difference (MacAdam Units)
Disperse Dyeings (D-Y-42, D-R-55, D-B-7)	UV lamp (air)	1	Std dyeing	-
		2	Reuse 1	3.0
		3	Reuse 2	3.3
		4	Reuse 3	1.9
Acid Dyeings (A-R-266, A-Y-19, A-B-25)	Ozonator (Air)	1	Std dyeing	-
		2	Reuse 1	5.2
		3	Reuse 2	6.1
		4	Reuse 3	9.2*
		5	Reuse 4	6.0
Actual Commercial Dyeing (Acid Dyes)	Ozonator (Air)	1	Dk Brown 1(Std)	-
		2	Dk Brown 2	3.4
		3	Dk Brown 3	5.8
		4	Lt Beige 4	2.4**

* Weighing error

** Compared to standard Lt. Beige dyeing

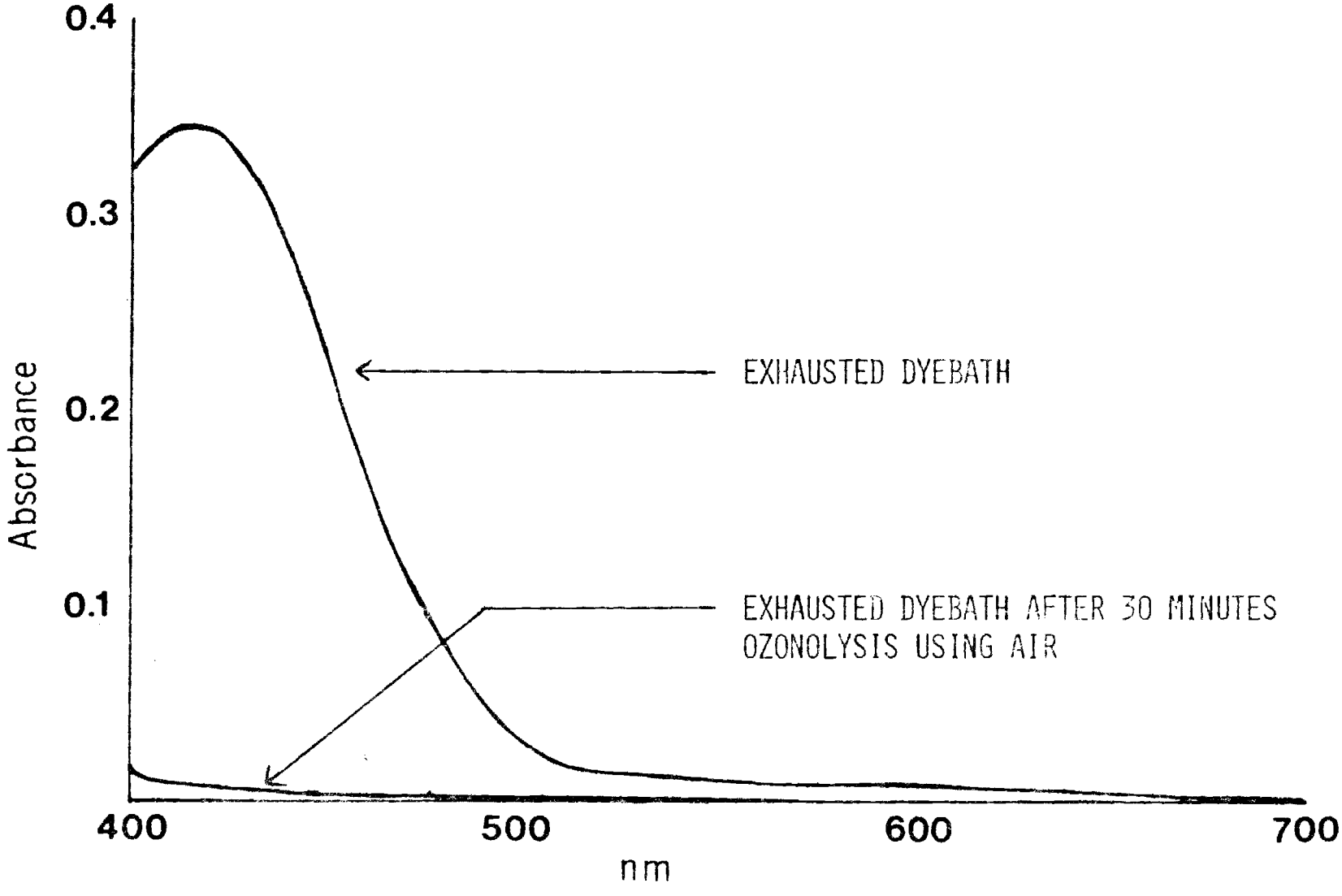


Figure 4. AIR OZONOLYSIS OF AN EXHAUSTED DYEBATH FOR 30 MINUTES.

This series of experiments suggests that the residual acid or disperse dyes in commercial exhausted dyebaths can be efficiently degraded to prepare the dyebath for reuse. Substantial savings in time, energy and chemicals can be realized with small initial capital investment.

IV. Actual Active Species Production

The actual mg of "ozone" or active oxygen species produced per hour has been determined for each of the 4 systems studied and results are shown in Figure 5. Oxygen passed through an ozonator has the highest production, 940 mgO_3/hr. Comparable values are obtainable for an ozonator operated with air and an ultraviolet lamp operated with oxygen. Only 35 mgO_3/hr. was produced from an ultraviolet lamp using air.

In Table 2 the efficiency of several different methods to produce active oxygen species is compared. The two methods that produce the highest amount of active species per watt-hour are the ozonator and UV lamp that employ a pure oxygen flow. The use of air decreases production of active species by a factor of 2 to 10. The most energy intensive combination is use of the ultraviolet lamp with air.

V. Future Work

Major effort next quarter will be directed toward analysis of data and preparation of the final report.

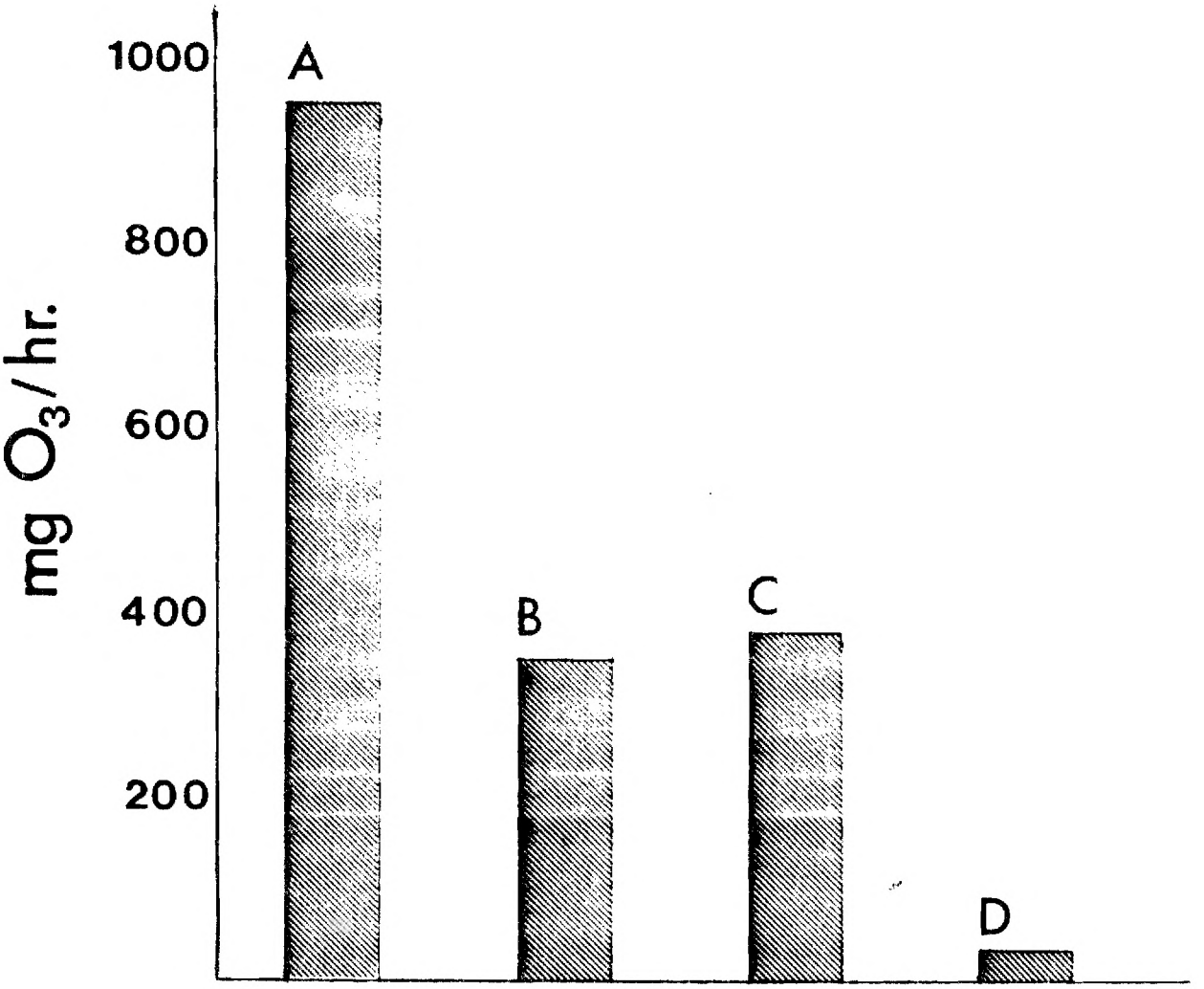


Figure 5. Actual Active Species Production

A - Ozonator with Oxygen
B - Ozonator with Air
C - UV Lamp with Oxygen
D - UV Lamp with Air

Table 2. Efficiency of Different Methods to Produce Active Oxygen Species

Method	mgO_3/hr	watts-usage	$mgO_3/watts$
Ozonator - oxygen	940	144	6.5
Ozonator - air	346	144	2.4
UV lamp - oxygen	374	68.4	5.5
UV lamp - air	35	68.4	0.5

TOWARD ZERO DISCHARGE FROM TEXTILE DYEING PROCESSES

E-27-673
Final Report

Wayne C. Tincher
Professor

Linn Averette
Research Technologist
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

INTRODUCTION

The textile industry uses approximately 125 billion gallons of water annually (1). Much of the process water is discharged with appreciable quantities of organic and inorganic chemicals (dyes, pH control agents, lubricants, surfactants, auxiliaries, oligomers, etc.) which require extensive treatment of the wastewater and which contribute to the pollution problems associated with textile processing. In the past, the textile pollution problem has been attacked by construction of waste treatment facilities. As requirements became more stringent, the waste treatment plant was expanded or additional treatment processes were added to meet the standards. This approach has consumed large sums of non-income-producing capital and has increased the operating costs of many textile plants. In addition, dyes present in textile processing wastewater are resistant to usual treatment procedures and constitute a particularly difficult problem for all treatment systems.

Two basic types of procedures are used for textile coloration -- pad-fix (continuous) processes and exhaust (batch) processes. Continuous dyeing is used primarily for long runs of a given fabric style. Because of their continuous nature and the use of relatively small volumes of dye liquor, these processes tend to be more efficient than batch processes. Exhaust batch processes are generally very inefficient in their use of chemicals, water and energy and generate large volumes of wastewater that must be treated. Despite these disadvantages, the versatility, ease of control, and short-run capability of exhaust processes enhance their desirability for coloration of many textile products.

In a conventional batch dyeing process the machine is filled with water, the goods to be dyed are entered, and the fabric moved through a bath (or a bath moved through the goods) to saturate the material with water. Chemical auxiliaries such as wetting agents, pH control agents, leveling agents, and chelating agents are then added to the bath followed by the dyes. The machine is heated from ambient to dyeing temperatures at a fixed rate (usually 3-4°F/min.) and held at the dyeing temperature for the time required to complete the dyeing. The goods being dyed are checked for proper shade, and if the shade has been attained, the dyebath is discharged to the drain. The goods are then post-scoured and/or rinsed to remove unfixed dye. The goods are removed from the machine, and the machine is refilled with water for the next load.

If the dyebath is examined before and after the dyeing cycle, two major changes have occurred: most of the dye has been removed from the bath by the yarn or fabric and the bath is hot rather than cold. Most of the auxiliary chemicals added to the bath are still present in the same

condition as they were at the start of the dyeing cycle. When the dyebath is discharged to the drain, large quantities of energy, water and useful chemicals are lost. A more reasonable procedure would be to analyze the spent dyebath for the remaining dye, to reconstitute the bath to the desired strength, and to reuse it for subsequent dyeings. Reuse of dyebaths was calculated to significantly reduce the energy, water and chemical requirements in batch dyeing, as well as reduce pollution loads.

For the past several years a major research program in the School of Textile Engineering at Georgia Tech has been directed toward evaluation of the technical and economic feasibility of reconstitution and reuse of dyebaths. In previous papers on the work the laboratory equipment (2-5) of the reuse system has been described and the actual demonstration of reconstitution and reuse of dyebaths in hosiery dyeing (6-7), carpet dyeing (8) and fabric dyeing (9) have been reported. The plant experiments showed that dyebath reconstitution and reuse could reduce water use and discharge by 64% in hosiery dyeing, 57% in carpet dyeing and 45% in fabric dyeing with no reduction in quality of the dyed fabric or increase in production problems.

Dyebaths can be reused routinely for five to ten dyeings but eventually the bath must be discarded when a light color must be dyed following a very dark color. The current work was undertaken to develop a system to decolorize and reuse baths from dyeing of dark shades so that further reuse of the dyebath would be possible. Ozone and/or excited "singlet" oxygen were selected for the decolorization studies. Both of these species have been previously demonstrated to be effective in destroying the color of dyes (10).

EXPERIMENTAL PROCEDURES

The dyes and chemical dyeing auxiliaries selected for study were ones commonly used in the coloration of nylon and polyester carpet. Since all commercial dyes contain substantial quantities of additives and impurities, it was necessary to purify dye samples prior to use. Standard techniques were used for purification.

Concentrations of dyes in solution were obtained by absorption spectrophotometry (11). Standard dye solutions were prepared by dissolving 1 gram of purified dye in 1 liter of distilled water. Other concentrations for preparing absorbance versus concentration curves were made by dilution of the 1 gram per liter standard solution.

The active oxygen species for decolorization of dyes were produced with the apparatus shown in Figure 1.

Ozone was produced by flowing either pure oxygen or air through a 9000 volt ozonator and then diffusing the active species through a used dyebath. Singlet oxygen was similarly obtained by passing pure oxygen or air around a short wavelength lamp.

The quantities of active species produced by the various systems were obtained by filling the gas bottles with 150 ml of standard potassium iodide solution and determining the active specie as ozone by the procedure given in Standard Methods (12). Early experiments on decolorization of dyes by the various techniques showed that ozone was more effective than "singlet" oxygen. Subsequent experiments were limited to ozone decolorization.

The quantities of ozone required to decolorize each of seven dyes selected for initial study were determined quantitatively with the apparatus shown in Figure 1. In these experiments the dye solutions were placed in the first gas bottle of the bottom series and potassium iodide solution in the other five bottles. Equal flow was maintained in the three series of bottles so that the total ozone produced can be determined from the top row and the quantity of ozone required to decolorize the dye from the bottom row. Typical results for two acid dyes commonly used for dyeing nylon carpet are shown in Figure 1. In general the results showed that a quantity of ozone roughly equivalent to the weight of the dye in solution was required to decolorize acid and basic classes of dyes. Disperse dyes used to dye polyester carpet required much larger quantities of ozone as can be seen from Figure 3.

Since dyebaths are generally hot at the end of the dyeing cycle, the effect of temperature on decolorization was also explored. At 80°C, acid dyes required approximately 30% greater quantities of ozone for decolorization. Disperse dyes were more easily decolorized at elevated temperatures as shown in Figure 3. The greater solubility of disperse dyes at 80°C is probably responsible for this increased efficiency of decolorization.

In addition to dyes, spent dyebaths will have appreciable quantities of auxiliary chemicals added to control the dyeing process. These chemicals will also react with ozone and the rate of reaction compared to ozone reaction with dyes will be an important consideration in the economic evaluation of ozone decoloration and dyebath reuse.

Two typical auxiliary chemicals were selected for study. Avitone T (duPont) is an anionic surfactant used as a dispersing agent for disperse dyes. Chemcogen 12LD (Chemical Processing of Georgia) is a typical anionic type leveling agent used in acid dyeing of nylon carpets. Results of the exposure of these two auxiliary chemicals to ozone at room temperature (25°C) are shown in Figure 4.

Results of the sudy of effects of ozone on auxiliary chemicals were encouraging since they indicate that these types of compounds react more slowly with ozone than the dyes. They should, therefore, have a low ozone demand during dye decoloration and substantial quantities of the auxiliary chemicals should be recyclable in the process.

DYEING IN RECYCLED BATHS

The possible effects of ozone decolorization of waste dyebaths on the carpet dyeing process was investigated in three series of dyeing experiments.

Nylon Carpet Dyeings

Nylon carpet samples dyed with a mixture of acid and basic classes of dyes were selected for initial studies. The nylon carpet samples were prescoured to remove fiber lubricants, identification tints, etc. A 50 gram sample of the carpet was placed in a beaker and 1.5 liters of water (liquor ratio of 30:1) were added. A leveling agent, pH control agent, and three dyes, Acid Red 151, Acid Blue 40 and Basic Yellow 11 were added to the bath. The temperature was raised to 100°C at 2°C per minute and held at 100°C for fifteen (15) minutes. Acetic acid was added to adjust the pH to 4.5 and the dyeing continued for thirty (30) additional minutes. The carpet was removed from the beaker and rinsed and afterscoured.

The residual dyebath was then exposed to ozone to decolorize the remaining dyes. The dyebath was used for five (5) consecutive dyeings before being discarded. The quantities of ozone actually required for dyebath decoloration was very close to the amount calculated from the residual dye concentration and the ozone dye decoloration curves previously obtained.

The five samples of nylon carpet dyed consecutively in the same dyebath by decolorizing with ozone and reuse of the bath were evaluated for color reproducibility, stability of the color to light exposure (lightfastness), colorfastness to water exposure, and colorfastness to abrasion (crockfastness) (13). Standard exposure conditions and evaluation procedures were used to assess the quality of the dyeings in recycled baths.

Results of the color reproducibility study are shown in Table 1. Color differences between the first dyeing (in a fresh bath) and the four subsequent dyeings (in the recycled bath) were calculated using the Friele-MacAdam-Chickering equation (FMC-II) (14). In this system, one unit of color difference is a just perceptible color difference to the average observer. All color differences for the acid and basic dyed nylon were within acceptable ranges for commercial production of nylon carpets. Colorfastness of the dyeings were also acceptable.

Polyester Carpet Dyeings

Polyester carpet samples were dyed with disperse dyes in a manner similar to the nylon carpet dyeings described previously. A large piece of polyester carpet was prescoured to remove fiber lubricants, identification tints, etc. A 50 gram samples of the carpet was placed in a 5-liter beaker and 1.5 liters of water (liquor ratio of 30:1) were added. A dye dispersing agent, a pH control agent, and three dyes, Disperse Yellow 42, Disperse Red 60 and Disperse Blue 7 were added to the bath. The pH was adjusted to 5.0 with acetic acid and a dye carrier, (10% owf or 5 grams) was added. The temperature was raised to 100°C and maintained for one hour. The carpet sample was then removed from the beaker, rinsed with warm water, afterscoured, and dried at 120°F for one hour.

The used dyebath was then exposed to ozone to decolorize the residual dyes. The bath was then reconstituted to its original volume and used for the next dyeing. Five dyeings were carried out in the same bath.

As noted for the nylon carpet dyeings, the actual ozone requirements were very similar to the calculated requirements based on dye decolorization experiments carried out earlier.

The polyester carpet samples were also tested for color reproducibility and colorfastness.

Somewhat larger color differences of the order of 5 or 6 FMC II units are observed for the polyester dyeings in recycled baths. Apparently during the decolorization of waste dyebaths containing disperse dyes, oxidation by-products are formed and accumulate which can oxidize a portion of the dyes added for the subsequent dyeing. The color difference increases for each dyeing run if the decolorized dyebath is reused without being reduced (run 2-5).

In order to correct this problem a sixth run was made in the spent

dyebath using a small amount of a reductant, $Na_2S_2O_4$, (sodium hydrosulfite is a common reductant used in textile operations) prior to the added dye and sample 6 is well within acceptable color difference limits. This procedure would probably be required in production use for polyester dyeings.

Colorfastness results were comparable for both the sample dyed in the initial bath and samples dyed in the recycled baths.

Combined Reconstitution and Ozone Decolorization

In the final study the combination of reconstitution and reuse of dyebaths with ozonation and continued reuse was investigated using the formulation of actual commercial dyeings. A standard dark brown dyeing was carried out using nylon carpet, followed by two dark brown dyeings. These first two reuses were accomplished by analyzing the spent dyebath for residual dye, then replenishing the bath with the required amount of dyes and chemicals and then dyeing the next sample. For the fourth dyeing, the spent dyebath was treated with active oxygen species produced by the ozonator using air until no color remained. For a rigorous test of the active species degradation, a light beige sample was dyed as the third reuse. The color difference between the third reuse and a standard light beige sample was very acceptable, being only 2.4 FMC II units (see Table 1).

CONCLUSIONS

Results of the study have led to a number of important conclusions about decolorization and reuse of dyeing wastewater.

1. Acid/basic dyes can be readily destroyed by treatment with ozone. Disperse dyes can also be destroyed but require a larger quantity of ozone.

2. Textile auxiliaries are not as rapidly destroyed as dyes by ozone. It should be possible, therefore, to destroy the color and reuse both the water and a substantial quantity of auxiliary chemicals.

3. Nylon carpet can be dyed in recycled baths that have been decolorized by ozone. Carpets dyed in recycled baths are of acceptable commercial quality.

4. Polyester carpet can be dyed acceptably in ozone decolorized baths if the bath is treated with a reductant prior to reuse.

5. Ozone decolorization can be combined with reconstitution and reuse systems to permit dyeing of lighter shades after darker shades in spent dyebaths.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of this work by the Office of Water Research and Technology.

REFERENCES

1. Anonymous, "In-Plant Control of Pollution: Upgrading Textile Operations to Reduce Pollution", Technology Transfer Seminar Publication EPA-62513-74-004, Environmental Protection Agency,

Washington, D.C. 1974.

2. Tincher, W. C., Conservation of Water, Chemicals, and Energy in Dyeing Nylon Carpet, Final Technical Report ERC-07-77, Office of Water Research and Technology Project No. A-064-GA, Georgia Institute of Technology, Atlanta, Georgia, November 1977.

3. Tincher, W. C., American Dyestuff Reporter, Vol. 66, No. 5, May 1977, p. 36.

4. Cook, F. L. and Tincher, W. C., Textile Chemist and Colorist , Vol. 10, No. 1, January 1978, p. 1.

5. Cook, F. L. and Tincher, W. C., "Energy Conservation in Textile and Polymer Processing", ACS Symposium Series, No. 107, American Chemical Society, Washington, D.C., 1979, p. 201.

6. Cook, F. L., Tincher, W. C., et al., In-Plant Demonstration of Dyebath Reuse Applied to Hosiery Dyeing, Final Technical Report Department of Energy Project No. EY-76-S-05-5099, Georgia Institute of Technology, Atlanta, Georgia, April, 1979.

7. Cook, F. L., Tincher, W. C., et al., Textile Chemist and Colorist, Vol. 12, Nov. 1, January 1980, p. 1.

8. Tincher, W. C., Cook, F. L., et al., In-Plant Demonstration of Energy Optimization in Beck Dyeing of Carpet, Final Technical Report Department of Energy Project No. DE-AS05-76CS4008, Georgia Institute of Technology, Atlanta, Georgia, July, 1980.

9. Tincher, W. C., Cook, F. L. and Barch, L. A., "Reusing Dyebaths in Jet Dyeing", American Association of Textile Chemists and Colorists Technical Conference, Charlotte, North Carolina, October, 1981.

10. Perkin, W. S., Judkins, J. F., and Perry, W. D. "Renovation of Dyebath Water by Chlorination or Ozonation" Textile Chemist and Colorist, Vol. 12, No. 8, August, 1980, p. 102.

11. Willard, H. H., Merritt, L. L., and Dean, J. B., Instrumental Methods for Analyses, 4th Edition, Van Nostrand Rinehold Company, New York, 1965, P. 77ff.

12. Standard Methods for the Examination of Water and Wastewater, 13th edition, APAA-ANND-NPCF, Washington, D.C., 1975, p.271.

13. "Colorfastness to Crocking: AATCC Crockmeter Method", AATCC Test Method 8-1977, Technical Manual of the American Association of Textile Chemists and Colorists, Vol. 57, 1978, p. 132.

14. Judd, D. B. and Wyszecki, G., Color in Business, Science , and Industry, 3rd edition, John Wiley and Sons, New York, 1975, p. 322.

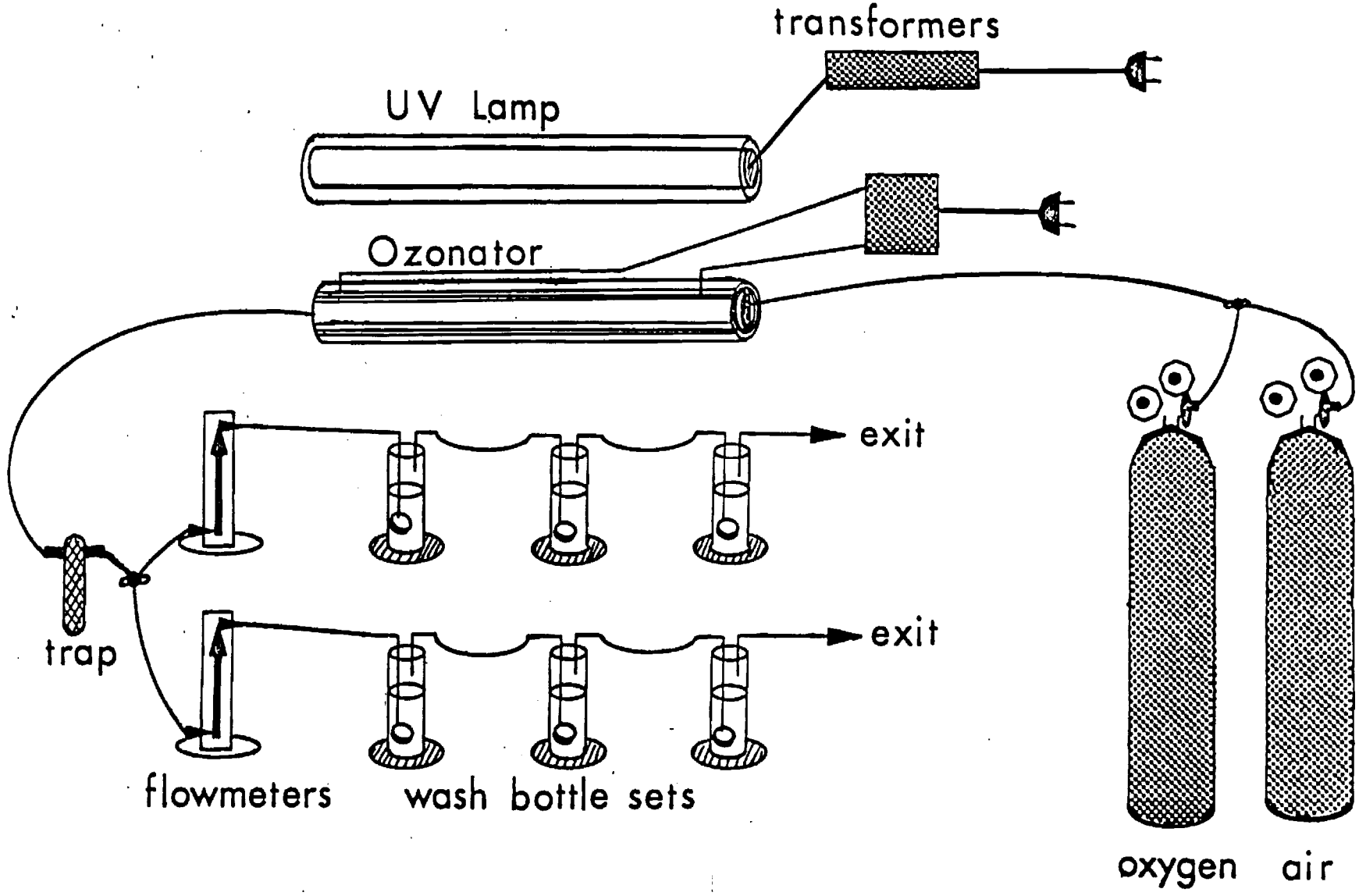


Figure 1. Ozone/Singlet Oxygen Apparatus

Table 1. Color Reproducibility From Run to Run Ozone Decolorization

Sample		DE (FMC II Units)
Acid Dyed Nylon Std.	No. 1	-
Sample	No. 2	3.3
	No. 3	3.8
	No. 4	3.9
	No. 5	3.0
Basic Dyed Nylon Std.	No. 1	-
Sample	No. 2	3.6
	No. 3	2.8
	No. 4	3.8
	No. 5	3.7
Polyester Std.	No. 1	-
Sample	No. 2	2.3
	No. 3	2.0
	No. 4	4.9
	No. 5	6.4
	No. 6	0.3
Nylon Reuse Std.	Dk. Brown	-
	Dk. Brown	3.4
	Dk. Brown	5.8
	Lt. Beige	2.4*

* Compared to standard light beige dyeing.

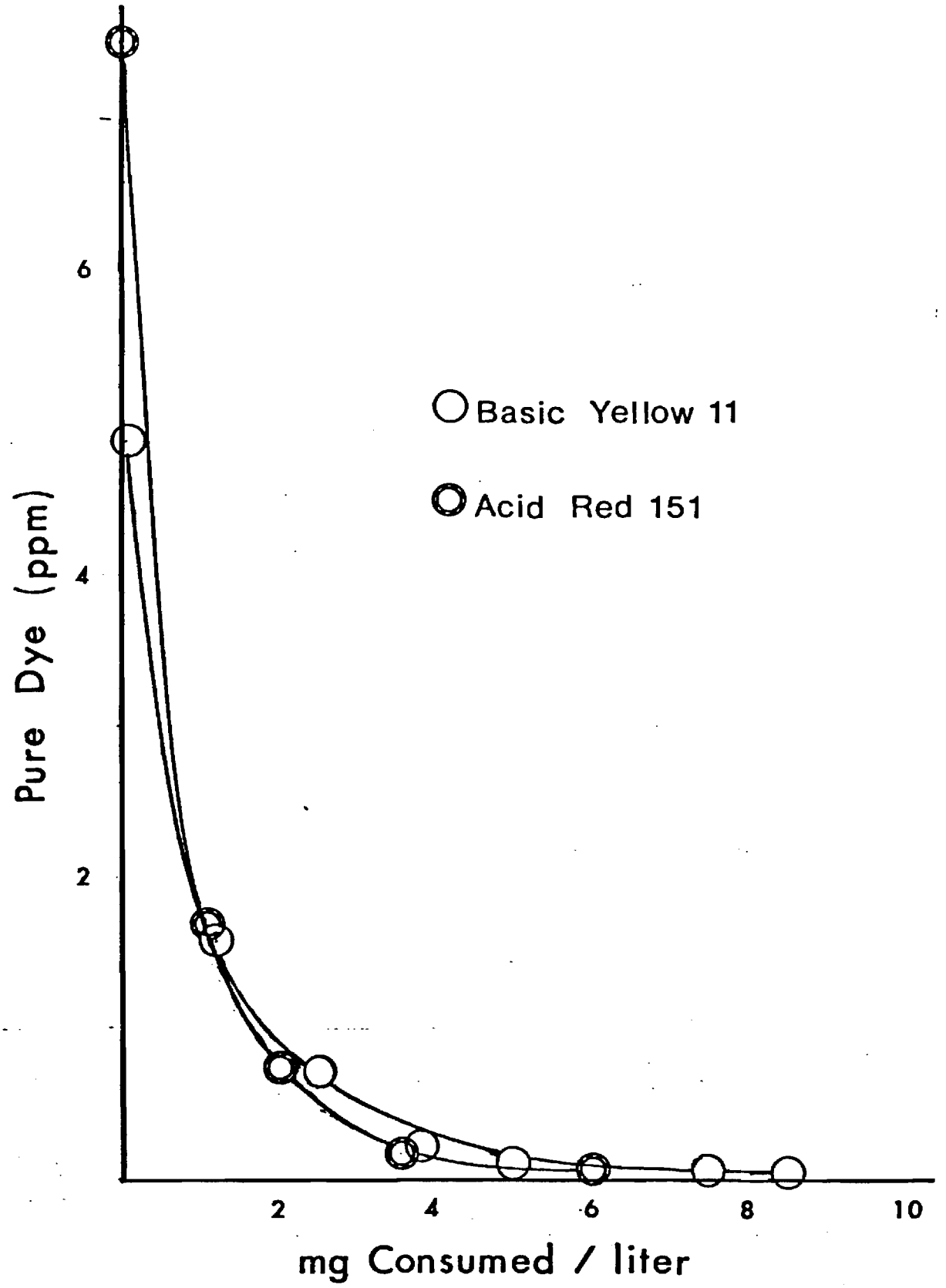


Figure 2. Dye Decolorization by Ozone.

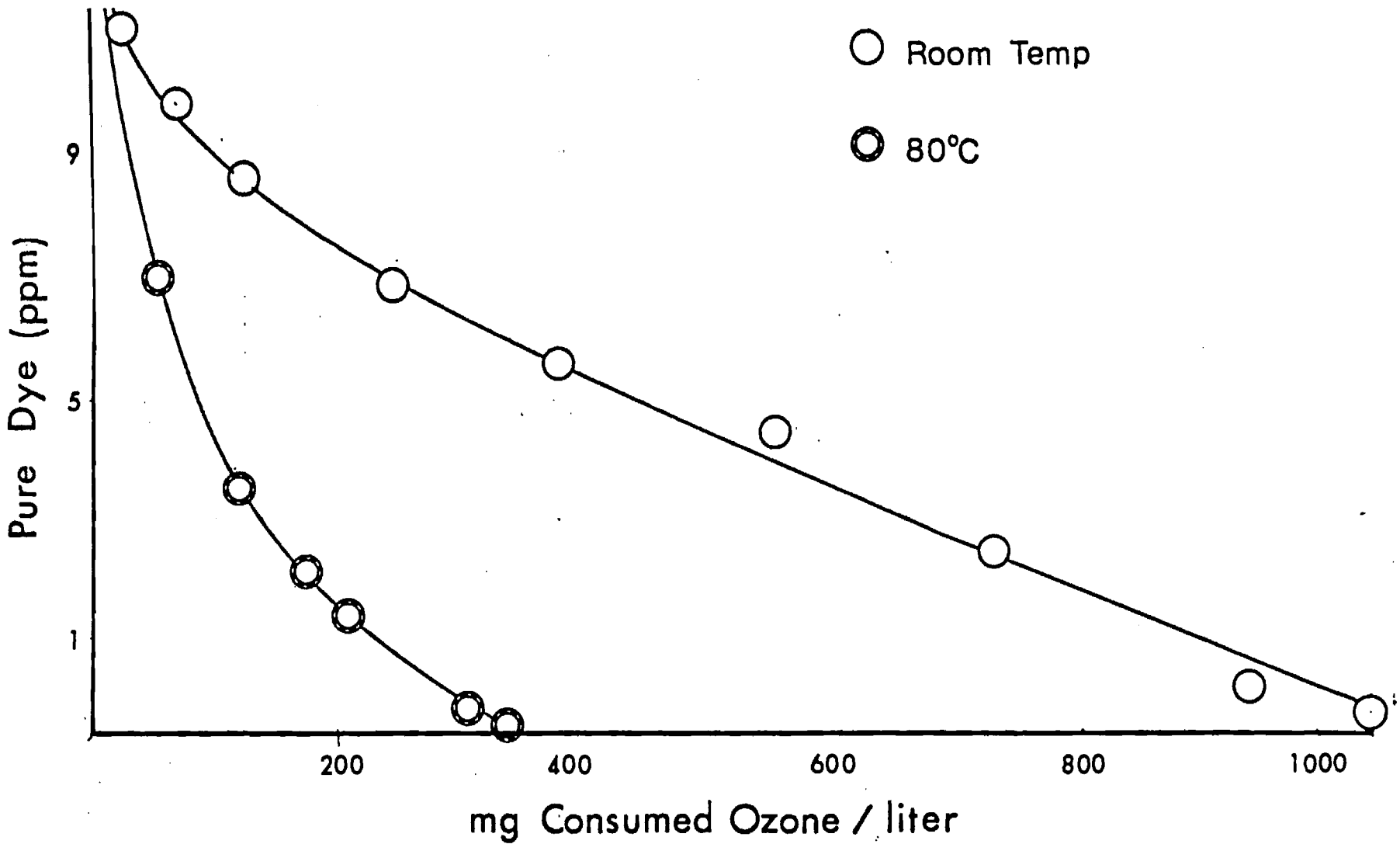


Figure 3. Ozone Decolorization of Disperse Yellow 42.

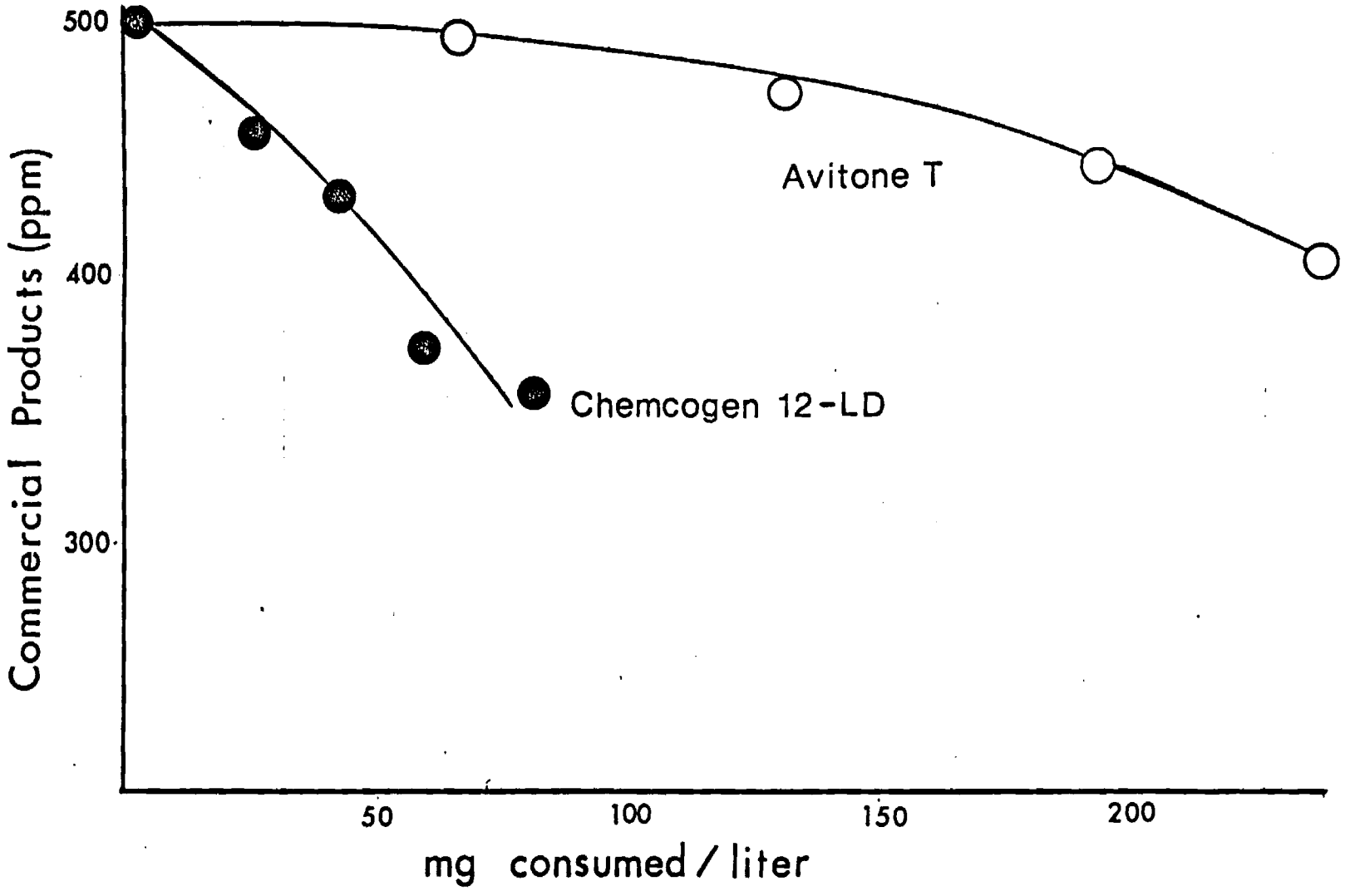


Figure 4. Ozone Oxidation of Auxiliaries